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United States
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Agency

Laboratory
Research Triangle Park NC 27711

February 1979

Proceedings of the Third Stationary Source Combustion Symposium; Volume II. Advanced Processes and Special Topics

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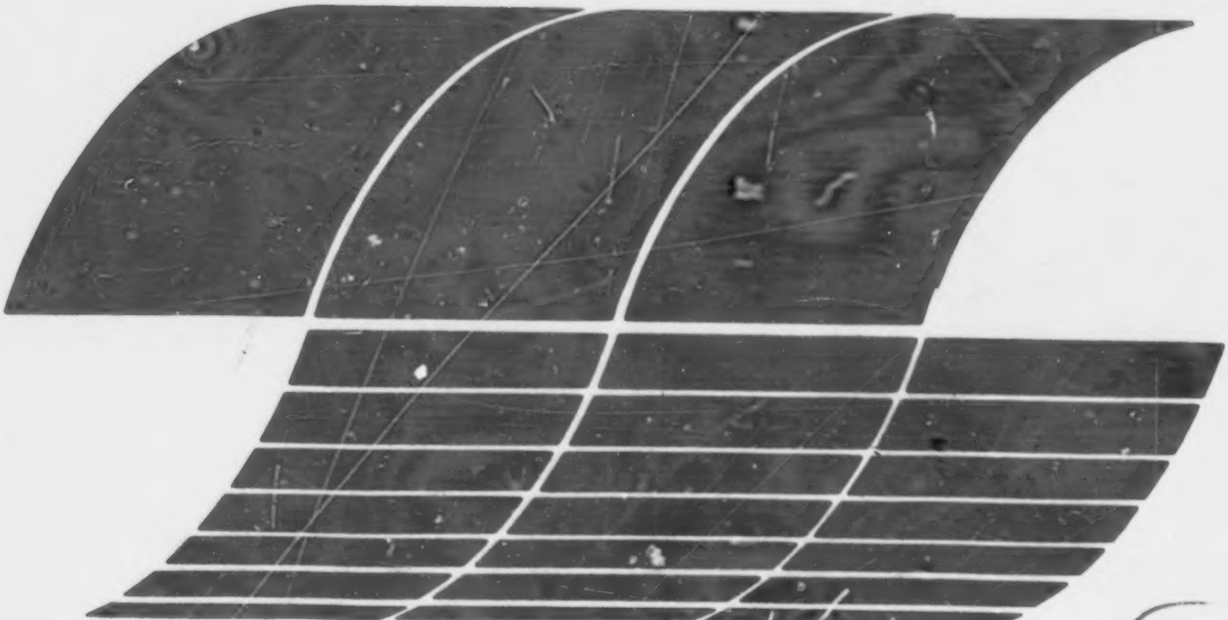

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4. Environmental Monitoring
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February 1979

Proceedings of the Third Stationary Source Combustion Symposium;
Volume II. Advanced Processes and Special Topics

Joshua S. Bowen, Symposium Chairman,
and
Robert E. Hall, Symposium Vice-chairman

Environmental Protection Agency
Office of Research and Development
Industrial Environmental Research Laboratory
Research Triangle Park, North Carolina 27711

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Office of Research and Development
Washington, DC 20460

PREFACE

These proceedings document more than 50 presentations and discussions presented at the Third Symposium on Stationary Source Combustion held March 5-8, 1979 at the Sheraton Palace Hotel, San Francisco, California. Sponsored by the Combustion Research Branch of the EPA's Industrial Environmental Research Laboratory - Research Triangle Park, the symposium papers emphasized recent results in the area of combustion modification for NO_x control. In addition, selected papers were also solicited on alternative methods for NO_x control, on environmental assessment, and on the impact of NO_x control on other pollutants.

Dr. Joshua S. Bowen, Chief, Combustion Research Branch, was Symposium Chairman; Robert E. Hall, Combustion Research Branch, was Symposium Vice-Chairman and Project Officer. The welcoming address was delivered by Clyde B. Eller, Director, Enforcement Division, U.S. EPA, Region IX and the opening Address was delivered by Dr. Norbert A. Jaworski, Deputy Director of IERL-RTP.

The symposium consisted of seven sessions:

Session I: Small Industrial, Commercial and Residential Systems
Robert E. Hall, Session Chairman

Session II: Utilities and Large Industrial Boilers
David G. Lachapelle, Session Chairman

Session III: Advanced Processes
G. Blair Martin, Session Chairman

Session IV: Special Topics
Joshua S. Bowen, Session Chairman

Session V: Stationary Engines and Industrial Process Combustion Systems
John H. Wasser, Session Chairman

Session VI: Fundamental Combustion Research
W. Steven Lanier, Session Chairman

Session VII: Environmental Assessment
Wade H. Ponder, Session Chairman

SESSION III:

ADVANCED PROCESSES

G. BLAIR MARTIN
CHAIRMAN

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THE INFLUENCE OF FUEL CHARACTERISTICS
ON NITROGEN OXIDE FORMATION
— BENCH-SCALE STUDIES

By:

M. P. Heap, D. W. Pershing, G. C. England, J. W. Lee, and S. L. Chen
Energy and Environmental Research Corporation
Irvine, California

ABSTRACT

Results of two bench-scale experimental studies are presented showing the effect of the physical and chemical characteristics of both liquid and solid fuels on fuel nitrogen conversion. The formation of thermal NO was prevented by the use of artificial oxidant mixtures ($Ar/CO_2/O_2$) free from molecular nitrogen. Results are presented showing the effect of fuel nitrogen content, initial fuel/air mixing process, and droplet/particle size for both staged and unstaged conditions. The effectiveness of staged combustion as an NO_x control technique appears to be dependent upon fuel nitrogen volatility.

ACKNOWLEDGEMENT

The authors are pleased to acknowledge the assistance of several of their colleagues, R. C. Horton, P. C. Lackey and J. Small in the conduct of the experiments and to G. B. Martin and W. S. Lanier of the Environmental Protection Agency for their support and encouragement.

SECTION 1

INTRODUCTION

Fossil fuels contain trace specie which may form pollutants during the combustion process, e.g., sulfur oxides, nitrogen oxides and fine particulate matter. The oxidation of chemically-bound nitrogen during the combustion of fossil fuels provides a significant source of nitrogen oxides, and sulfur emissions are directly related to the fuel sulfur content. Although this paper is concerned with the fate of fuel nitrogen, the studies from which the results are drawn include an assessment of fuel characteristics on the formation of other pollutants, particularly the size distribution and trace metal content of fine particulate emissions.

The combustion of coal and residual fuel oils accounts for the major fraction of nitrogen oxide emissions from stationary combustion sources, and since it is generally recognized that the oxidation of chemically-bound nitrogen contained in these fuels provides a significant fraction of the total emissions, the factors affecting the fate of fuel nitrogen compounds are of major importance in the development of low emission combustion systems. The nitrogen content of coals and petroleum varies considerably. Typical values range from 0.2 to 0.5 percent for residual fuel oils, and 1.1 to 1.7 percent by weight for coals although for both fuels examples can be found outside these ranges. Alternate liquid fuels derived from shale or coal have higher nitrogen contents than conventional petroleum-derived liquid fuels and thus, have the potential to produce significant nitrogen oxide emissions if burned without the application of control techniques.

An effective method of controlling NO_x emissions from combustors fired with nitrogen-containing fuels is to modify the combustion process in such a way as to ensure that heat release occurs in two stages. Initially, the fuel reacts under oxygen-deficient conditions which serves to maximize the production of N_2 from the bound fuel nitrogen specie. Then, provided heat is lost from the first stage, NO production during burnout in the second stage is minimized. The optimum design of a staged combustor requires a knowledge of the fate of the fuel-bound nitrogen as a function of the characteristics of the fuel and the combustion process.

The effect of combustion on the fate of nitrogen contained in solid and liquid fuels is illustrated by the simplified flowchart shown in Figure 1. Before combustion can take place it is necessary that the fuel undergo some physical transformation to enhance combustion rates by providing for efficient fuel/air mixing. Coal will be pulverized or crushed external to the combustor, and liquid fuels are injected through a nozzle which atomizes the liquid, providing a spray of small droplets. The combustion of liquid or solid fuels in turbulent diffusion flames can be conveniently divided into three processes.

- Devolatilization - As the fuel is heated, matter is driven from the particle or droplet in the form of a gas or tar which may undergo secondary pyrolysis reactions producing carbonaceous solids.
- Gaseous Combustion - The gaseous fuel components are burned when they contact oxygen, provided conditions are suitable for ignition.
- Solid Burnout - The char remaining after devolatilization and any solid produced by pyrolysis reactions in the gas phase are oxidized. The fraction of nitrogen contained in the fuel which is converted to nitric oxide will depend upon the availability of oxygen during the combustion of the gaseous and solid components.

It is generally recognized that fuel nitrogen can be considered in two fractions: that which can be released from the fuel in the devolatiliztion process (volatile fuel nitrogen), and that which remains with the solid (refractory or char nitrogen). The relative amounts of volatile and char nitrogen will depend upon the droplet/particle heating rate and their final temperature. The division of fuel nitrogen into two components is complicated by the fact that volatile nitrogen fractions may undergo pyrolysis reactions where some of that nitrogen remains with the carbonaceous residue, and is not converted to a simple nitrogenous gaseous molecule.

The major factors governing the conversion of gaseous nitrogenous specie to NO are well-known, whereas char nitrogen reactions are less well-understood. However, it appears that in turbulent diffusion flames char nitrogen conversion to NO is low. Staged combustion processes attempt to provide a fuel-rich zone with optimum conditions to maximize the conversion of fuel nitrogen compounds to molecular nitrogen because these specie may form NO during the second stage burnout. An optimized rich first stage for minimum NO_x emissions will prevent char nitrogen from entering the burnout zone since conversion to NO in that zone will be small but finite, and provide the appropriate gas phase stoichiometry and residence time to minimize the content of gaseous nitrogenous specie. If the first stage is too rich, then the formation of HCN and NH_3 is favored; whereas if the first stage is too lean NO itself will enter the burnout zone. Thus, the two factors which will control the design of the rich first stage of a low NO_x combustor are those which pertain to the partition of fuel nitrogen between the volatile and char nitrogen fractions, and the kinetics (either homogeneous or heterogeneous) involved in the production of N_2 from nitrogneous species.

This paper describes a series of bench-scale experiments designed to identify the influence of both the chemical and physical characteristics of fuels on fuel nitrogen conversion to NO with the objective of building a data base which will allow combustor designers to assess the effect of fuel characteristics on pollutant emissions. The data base will be extended to include development studies and field tests using the same fuels. Consequently, a body of data will be assembled which will relate the influence of scale, combustion condition and fuel characteristics to pollutant emissions.

SECTION 2

APPROACH

The combustion of fossil fuels allows the production of nitric oxide from two sources. In order to assess the conversion of fuel nitrogen to NO, it is necessary to eliminate or estimate the production of NO from molecular nitrogen (thermal NO). Various investigators have used different techniques to achieve this objective. The addition of cooled combustion products (FGR) to the combustion air has been used as a method of eliminating thermal NO production with nitrogen-containing fuels (1), or emissions from a non-nitrogen-containing fuel have been used to assess thermal NO production (2). In this study thermal NO production was prevented by the use of artificial oxidants which did not contain molecular nitrogen, thus any NO appearing in the exhaust was formed either directly or indirectly from the nitrogen contained in the fuel. The artificial oxidant consisted of mixtures of argon, carbon dioxide, and oxygen to give the appropriate oxygen concentration and adiabatic flame temperature. This method is not free from criticism and has two major drawbacks:

1. The formation of fuel NO may be affected by the large excess of nitrogen molecules present when air is used as the oxidant.
2. The addition of CO_2 which is used to balance flame temperatures because of the different heat capacities of argon and nitrogen may affect H, OH and O concentrations and this affect is most likely to have a strong influence under fuel-rich conditions.

Although the use of artificial oxidants may not be ideal, it probably represents the most suitable method of assessing fuel nitrogen conversion during the combustion of real fuels.

EXPERIMENTAL SYSTEMS

Liquid and solid fuels were burned in two separate, but similar, refractory down-fired tunnel furnaces whose design has been described in detail elsewhere (3). The modular construction of both furnaces allowed ready access for flame observation and staged air injection through side-wall ports. Combustion air and artificial oxidant mixtures were supplied from a high pressure source and metered by 600 mm length rotameters, and they were preheated by electric circulation heaters. The furnace wall temperature was monitored continuously and when not in use, both furnaces were fired with propane to maintain their thermal equilibrium. Thermal NO production was found to be very strongly dependent upon furnace wall temperature, and it was necessary to learn by experience to match propane heat release patterns to those obtained with the test fuels to minimize experimental scatter.

The burner used in the liquid fuel furnace is shown in Figure 2, and several design iterations were necessary in order to provide a stable flame, and yet prevent coke buildup at the nozzle for the wide range of fuels investigated. Combustion air was introduced axially and its velocity could be varied by the use of interchangeable sleeves inserted in the burner throat. The interchangeable fuel injection system consisted of a 19 mm diameter stainless steel tube which contained the atomizing air supply tube, the fuel oil supply tube, a cartridge heater for final oil temperature control, and a chromal/alumel thermocouple positioned at the injector tip prior to the nozzle for accurate oil temperature measurement. The major portion of the experimental investigations carried out to date utilized a commercial ultrasonic oil atomizer (capacity 0.55 cc/sec) because it provided adequate atomization of the heavy fuel oils at relatively low flow rates. The tip of the fuel nozzle was positioned at the beginning of the burner divergent section, and in general, the visible flame front was displaced approximately one nozzle diameter from the nozzle tip. The liquid fuels were preheated electrically in a small supply tank drawn through a 60 micron filter into a variable-speed Zenith metering pump. The pump outlet pressure was maintained constant during calibration, and operation by means of a micro-needle valve. The oil flow rate was varied by direct mechanical adjustment of the pump speed.

Pulverized coal was supplied pneumatically from a hopper-fed screw feeder to one of two burners which allowed the coal to be burned entirely premixed or as a diffusion flame. Premixing was achieved by direct impingement of the coal jets with the main combustion air supply in a premixing chamber which was separated from the combustion zone via a series of water-cooled tubes which prevented flashback (see Figure 3). The coal/air mixture burned in a plug flow mode with the ignition zone situated in the refractory divergent. The coal, plus transport air could also be supplied to a variable swirl burner and injected either axially or radially; thus, allowing experiments to be conducted with very different fuel/air mixing rates. The variable swirl was achieved by dividing the total oxidant flow into two streams, one of which flowed axially around the fuel injector, and the other through fixed swirl vanes providing a tangential velocity component to the mixed flow. Details of the pulverized coal burners are presented in Figure 3.

The results presented in this paper all refer to exhaust measurements made under excess air conditions, and the same sampling and analysis system was used for both furnaces. It allowed for continuous monitoring of NO, NO_x, CO, CO_2, O_2, and SO_2. Flue gas was withdrawn from the appropriate exhaust duct through a water-cooled stainless steel probe. Sample conditioning prior to the instrumentation consisted of an ice bath water condenser, quartz wool filters, and a stainless/Teflon sampling pump. All sample lines were Teflon and stainless steel.

FUEL SELECTION

The characteristics of the liquid and solid fuels tested to date are presented in Tables I and II, respectively. The more significant fuel selection criteria were:

- Coals. Although the full range of coals selected has yet to be investigated, examples of each coal rank are to be tested, as well as variations in nitrogen and sulfur content within in each rank. Secondary criteria used in the selection process were oxygen-to-nitrogen ratio and the form of the sulfur (either organic or pyritic).

- Liquid fuels. The major selection criterion was the need to include residual fuels from the major crude sources available to U.S. consumers. Alternate fuels were used to extend the nitrogen content range. Future experiments will use fuels of widely different nitrogen mass evolution rates as a function of temperature.

SECTION 3

RESULTS

This section of the paper presents the results obtained to date for both liquid and solid fuels under normal and staged combustion conditions. The studies are far from complete, and therefore, only preliminary conclusions can be drawn from the results presented below. Whenever possible, liquid and solid fuels are presented in parallel in order to contrast the fate of fuel nitrogen in liquid and solid fuels.

FUEL NITROGEN CONTENT, UNSTAGED

Figures 4 and 5 show the emission of fuel NO and the conversion of fuel nitrogen to NO as a function of fuel nitrogen content for liquid and solid fuels, respectively. Both sets of results refer to 5 percent overall excess oxygen, and an air preheat level of 700°F. The results with coal were obtained with the premixed burner and a particle size distribution of 70 percent through 200 mesh. Combustor heat release rates were similar for all fuels. For liquid fuels, fuel NO emissions increased almost linearly with fuel nitrogen content. However, for the coals tested to date there is almost no effect of weight percent nitrogen on fuel NO emissions.

EFFECT OF FLAME ZONE TEMPERATURE, UNSTAGED

The flame zone temperature was varied by changing the carbon dioxide content of the artificial oxidant, while maintaining the oxygen concentration constant. The results presented in Figure 6 indicate that flame zone temperature has a much stronger influence on certain fuels than on others. In general, fuel nitrogen conversion in solid fuels is more strongly dependent upon the thermal environment than for liquid fuels, and certain coals show a very strong dependence upon temperature. These results can be attributed to the influence of heating rate and final temperature on the partition of fuel nitrogen between the volatile and the char fractions.

EFFECT OF INITIAL FUEL/AIR MIXING

Pulverized coal was burned in three modes in order to significantly modify the fuel/air contacting process, and Figure 7 shows the effect of the initial fuel/air mixing upon fuel NO formation for one coal as a function of excess oxygen. It can be seen that premixed conditions lead to the maximum conversion of fuel nitrogen to fuel NO, and that minimum conversions are obtained with an axial diffusion flame. The rate of mixing achieved in the radial swirling flame is intermediate between these two limits, and the fuel NO emissions are also between the premixed and the axial diffusion flame. This result is not unexpected and is in agreement with several other investigations (4,5), and can be attributed to the fact that as the coal/air mixing varies from premixed to an axial diffusion flame there is less oxygen in contact with the volatile fuel nitrogen fractions, and therefore, the formation of N_2 from the volatile nitrogenous specie is maximized. Figure 7 also shows that the effect of the initial fuel/air mixing conditions is also dependent upon the coal composition, and not all coals are as sensitive to fuel/air mixing rates as others which can be attributed to a variation in the split between volatile and char nitrogen fractions with coal type. Figure 8 shows the influence of the initial fuel/air mixing upon emissions from staged combustion systems with pulverized coal. These results are difficult to interpret because the actual rich first stage residence time will depend upon the fuel/air mixing type, but it appears that a backmixed first stage gives lower final emissions than either the premixed or the axial diffusion flame. These results were obtained using air as the oxidant because of the potential influence of CO_2 under fuel-rich conditions.

THE EFFECT OF PARTICLE/DROPLET SIZE

The influence of droplet size on the fate of fuel nitrogen in liquid fuels has been investigated by varying the atomizing air pressure to the ultrasonic nozzle, and by sieving the pulverized coal to burn narrow particle size distributions. Figures 9 and 10 show the effect of mean drop size on both fuel nitrogen conversion and thermal NO production for four liquid fuels. It appears that the fuel nitrogen conversion for alternate fuels is much less sensitive to liquid droplet size than for petroleum-derived fuels, where as drop size increases fuel nitrogen conversion decreases. Figure 10 shows there is a very strong influence of drop size on thermal NO production with an apparent maximum around a mean drop size of 30 microns. The ultrasonic atomizer was characterized under cold flow conditions using a laser diffraction system to determine both the mean and the drop size distribution of the spray as a function of liquid fuel flow rate, atomizing pressure, and liquid viscosity. These tests were carried out in a purpose built test rig and not with the actual oils used in the combustion tests (6).

Figure 11a shows that under premixed conditions fuel NO production from pulverized coal also decreases as particle size increases. However, as shown in Figure 11b, emissions under staged combustion conditions were lowest for the smallest particles.

SECTION 4

DISCUSSION

Heap (4) suggested that under rapid mixing unstaged combustion conditions volatile fuel nitrogen compounds were mainly responsible for the NO produced in pulverized coal flames, and that in order to minimize emissions it would be necessary to maximize the evolution of these volatile nitrogen compounds from the coal under fuel-rich conditions. It was suggested that fuel nitrogen conversion was highest when the volatile fuel nitrogen fractions were rapidly mixed with the available combustion air. Thus, nitrogen volatility would be a major factor in fuel nitrogen conversion to NO under normal combustion conditions. Figure 12 presents a composite plot of all fuels tested to date showing the fractional conversion of fuel nitrogen to NO as a function of weight percent nitrogen in the fuel. If the nitrogen is expressed on a dry-ash-free basis, then the conversions are much lower with coal than with any of the liquid fuels. This is entirely consistent with the hypothesis presented above, since it is known that some nitrogen remains with the char and there may not be an equivalence between char fractions for liquid and solid fuels. Figure 12 also contains one data point for a gaseous system (NH_3 in methane) which represents the extreme in nitrogen volatility. It can be seen that fuel nitrogen conversions are high.

Many of the results presented in the earlier section for coal can be explained in terms of an effect upon fuel nitrogen volatility. If heating rate and final temperature have a strong influence on the division of nitrogen between the refractory and volatile fractions, then either increase in temperature or decreasing particle size would tend to maximize the volatile nitrogen fraction, thus increasing fuel NO production under normal conditions. Conversely, if in a practical system char nitrogen could not be prevented from entering the second stage of a staged combustion system, then the use of fine particles would minimize NO emissions since the volatile nitrogen fraction would be maximized.

The effect of fuel nitrogen volatility with liquid fuels is much less pronounced under normal conditions. The Gulf Coast and the Alaskan oils appear to have the largest mass of refractory nitrogen assessed by comparing nitrogen mass evolution rates obtained under vacuum distillation, and yet their fractional fuel nitrogen conversion are somewhat higher than other oils. Also, pyridine is an extremely volatile nitrogen compound, and yet residual oils doped with pyridine to give the same nitrogen content as undoped residual fuels give very similar NO emissions to the undoped fuel (see Figure 13).

The normal combustion conditions used for the liquid fuels may be such that fuel volatility has little effect upon fuel NO conversion because the spray and air distribution give a well-dispersed rapidly mixed heterogeneous system which is relatively insensitive to the rate at which the fuel nitrogen compounds are released from the liquid drops. Under staged combustion conditions, however, if all of the nitrogen has not been vaporized in the rich stage then the effectiveness of staged combustion operation will be minimized. Experiments have been carried out with a range of liquid fuels which have different amounts of refractory nitrogen, i.e., that nitrogen which remains in a residual fraction after vacuum distillation. Figure 14 compares the effect of staged combustion on total NO emissions from several liquid fuels. Figure 15 compares the fractional reduction in NO_x emissions achieved under staged combustion conditions as a function of the fraction of the original nitrogen remaining in the residue for two residence times, and it can be seen that this parameter is remarkably effective in correlating the fractional reduction measured in the small-scale furnace.

SECTION 5

CONCLUSIONS

The results of the bench-scale studies on the fate of fuel nitrogen during the combustion of solid and liquid fuels indicate that:

- With liquid fuels, fuel nitrogen content is the primary composition variable affecting fuel NO formation. With coal, fuel nitrogen content may not be the primary variable controlling fuel NO production.
- Fuel NO_x formation appears to be relatively insensitive to thermal environment for both liquid and solid fuels burning in a diffusion flame, whereas there is a strong dependence of fuel NO production on flame temperature in premixed pulverized coal flames.
- Initial fuel/air contacting has a major impact upon fuel NO production under staged and unstaged conditions.
- With liquid fuels, minimum emissions under staged combustion conditions depend upon the amount of refractory nitrogen in the original fuel.

A major factor affecting the fate of fuel-bound nitrogen, and therefore, fuel NO production during fossil fuels combustion appears to be the relative volatility of the fuel nitrogen compounds. Early evolution of nitrogen compounds may maximize the benefits to be achieved from staged combustion, and although alternate liquid fuels contain significant quantities of fuel-bound nitrogen, NO_x control may not be difficult to achieve because the nitrogen compounds are volatile.

REFERENCES

1. Turner, D. W. and C. W. Siegmund. Staged Combustion and Flue Gas Recirculation: Potential for Minimizing NO_x Emissions from Fuel Oil Combustion. Presented at the American Flame Research Committee Flame Days, Chicago, Illinois, September 6-7, 1972.

2. Appleton, J. P. and T. B. Heywood. The Effects of Imperfect Fuel-Air Mixing in a Burner on NO Formation from Nitrogen in the Air and the Fuel. Fourteenth Symposium on Combustion, published in The Combustion Institute, Pittsburgh, Pennsylvania, 1973.

3. Pershing, D. W., J. E. Cichanowicz, G. C. England, M. P. Heap, and G. B. Martin. The Influence of Fuel Composition and Flame Temperature on the Formation of Thermal and Fuel NO_x in Residual Oil Flames. Presented at the Seventeenth Symposium (International) on Combustion, Leeds, England, 1978.

4. Heap, M. P., T. L. Lowes, R. Walmsley, H. Bartelds and P. LeVaguerese. Burner Criteria for NO_x Control Volume I Influence of Burner Variables on NO_x in Pulverized Coal Flames. EPA-600/2-76-061a, March, 1976.

5. Wendt, J. O. L., J. W. Lee and D. W. Pershing. Pollutant Control Through Staged Combustion of Pulverized Coal. U.S. DOE Report No. 1817-4, U.S. DOE Technical Information Center, Oak Ridge, Tennessee, 1978.

6. England, G. C., M. P. Heap, R. C. Horton, D. W. Pershing and G. Flament. The Effect of Fuel Properties and Atomizer Design on Emission Control from Heavy Fuel Oil Fired Combustors. Paper presented at the Third Stationary Source NO_x Symposium, San Francisco, California, March, 1979.

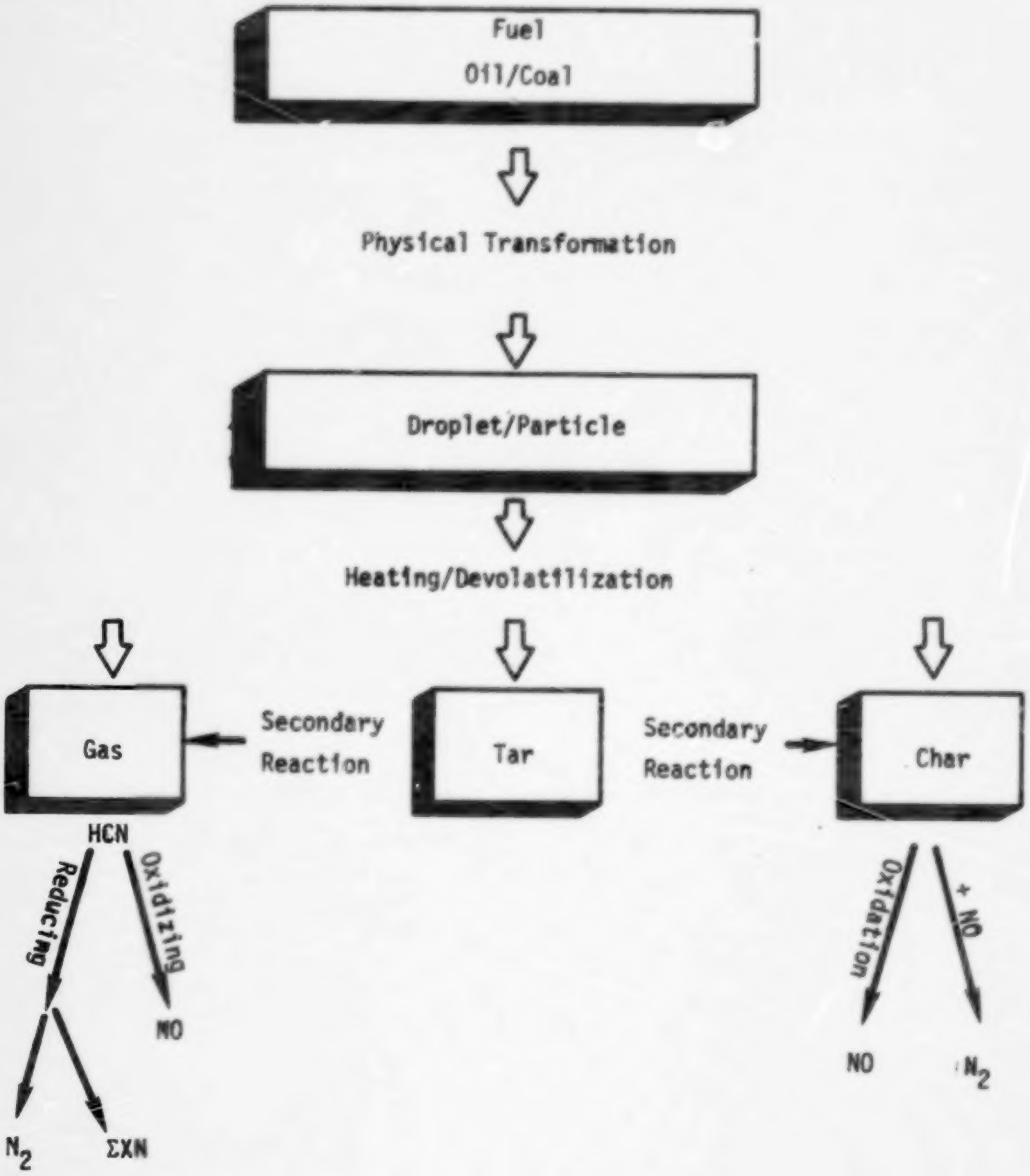
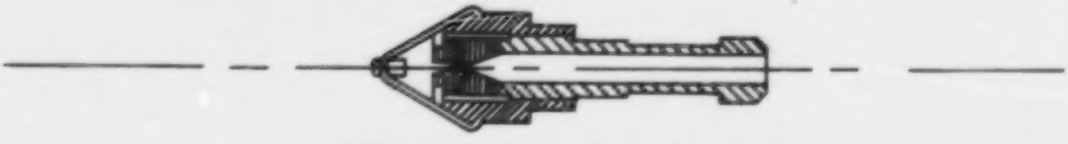
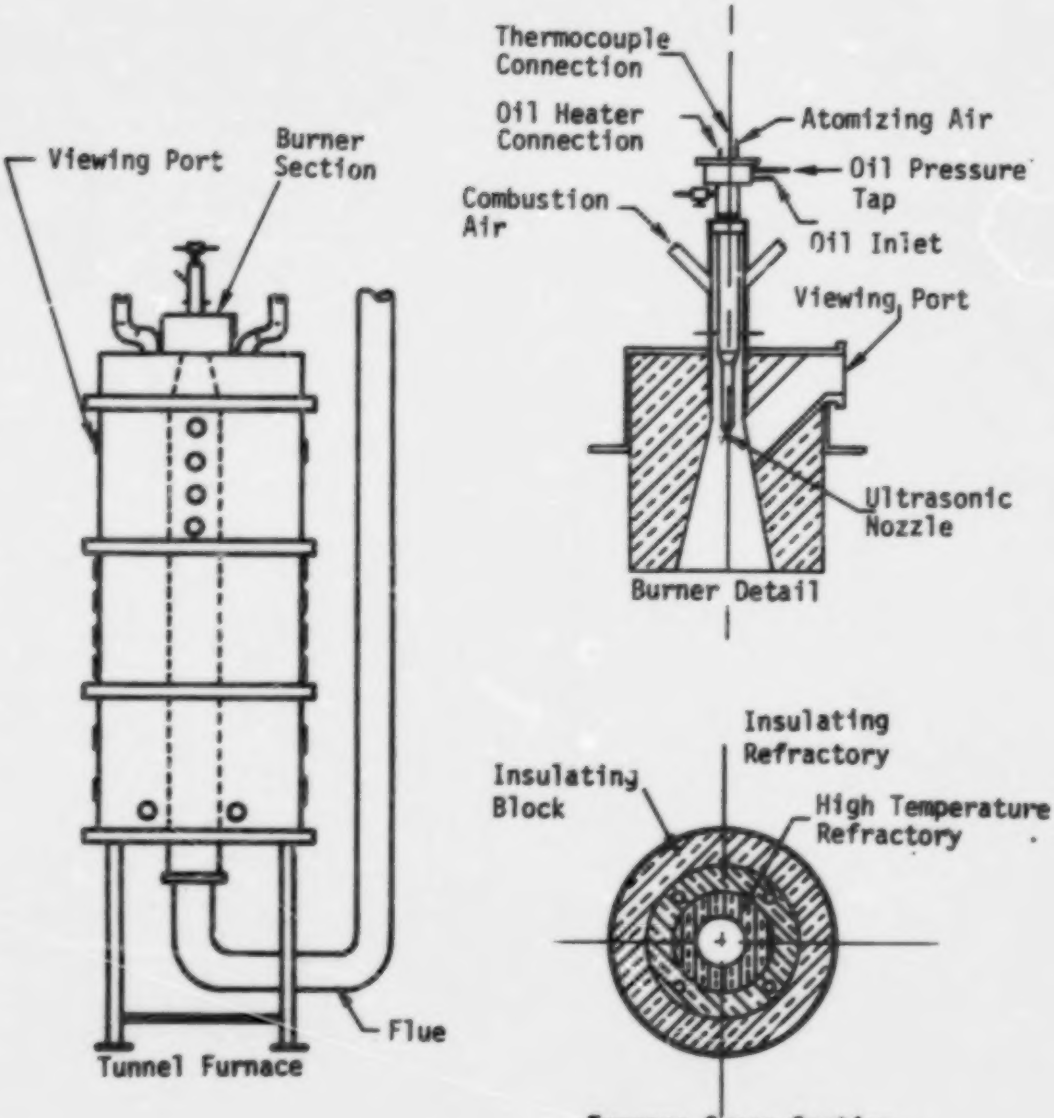

Fuel
Oil/Coal
Physical Transformation
Droplet/Particle
Heating/Devolatilization
Gas
Secondary Reaction
Tar
Secondary Reaction
Char
HCN
Reducing
Oxidizing
NO
N_2
ΣXN
Oxidation
+ NO
NO
N_2

Figure 1. The Fate of Nitrogen in Solid or Liquid Fuels During Combustion.



Ultrasonic Twin-fluid Atomizer



Viewing Port
Burner Section
Flue
Thermocouple Connection
Oil Heater Connection
Atomizing Air
Oil Pressure Tap
Combustion Air
Oil Inlet
Viewing Port
Ultrasonic Nozzle
Insulating Refractory
Insulating Block
High Temperature Refractory

Tunnel Furnace

Burner Detail

Furnace Cross-Section

Figure 2. Details of Liquid Fuel-Fired Furnace System.

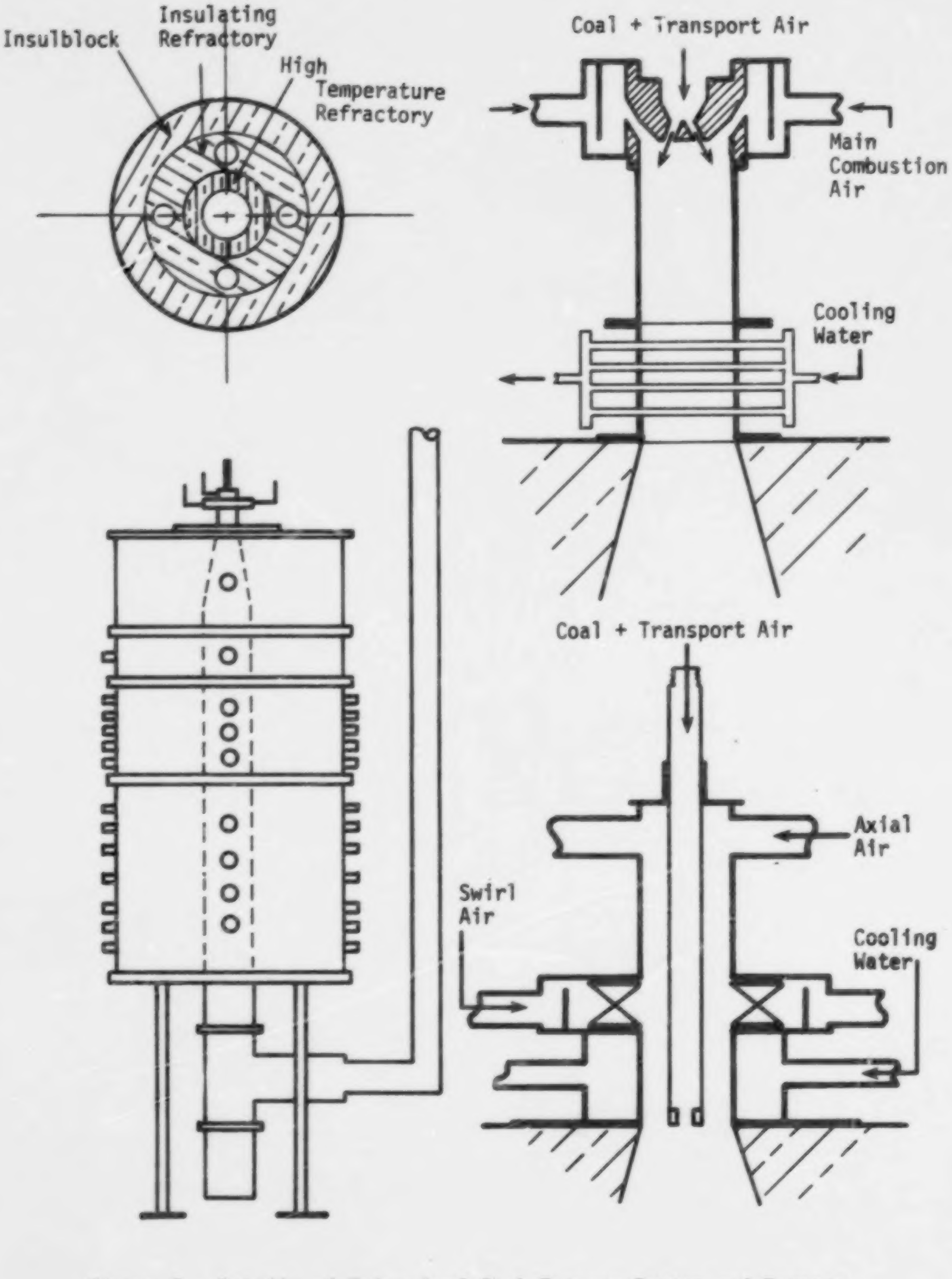

Insulblock
Insulating Refractory
High Temperature Refractory
Coal + Transport Air
Main Combustion Air
Cooling Water
Coal + Transport Air
Axial Air
Swirl Air
Cooling Water

Figure 3. Details of Pulverized Coal Furnace System and Burners.

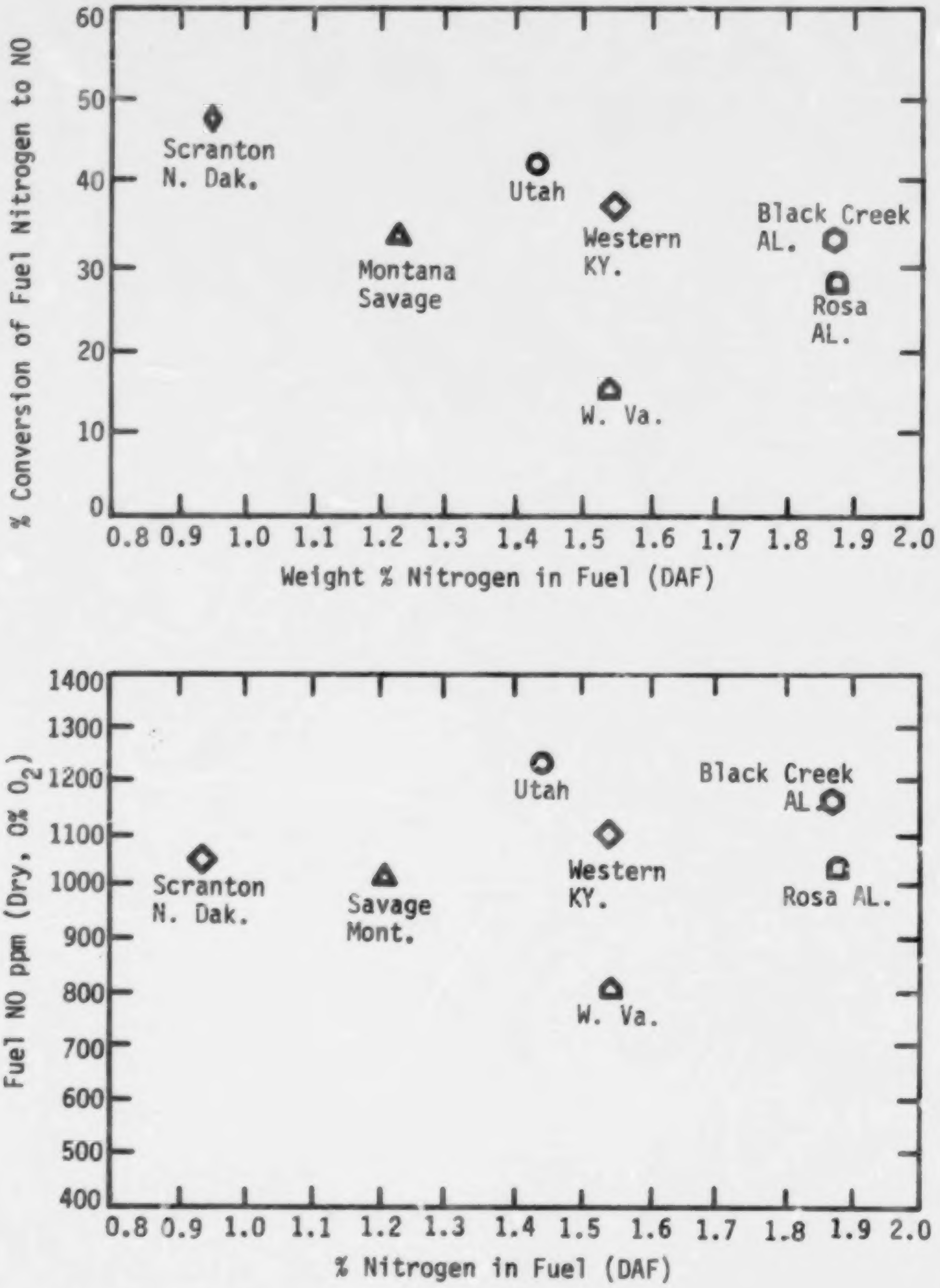


Figure 4. Fuel NO and Percent Conversion of Fuel Nitrogen to Fuel NO - Pulverized Coal Premixed.

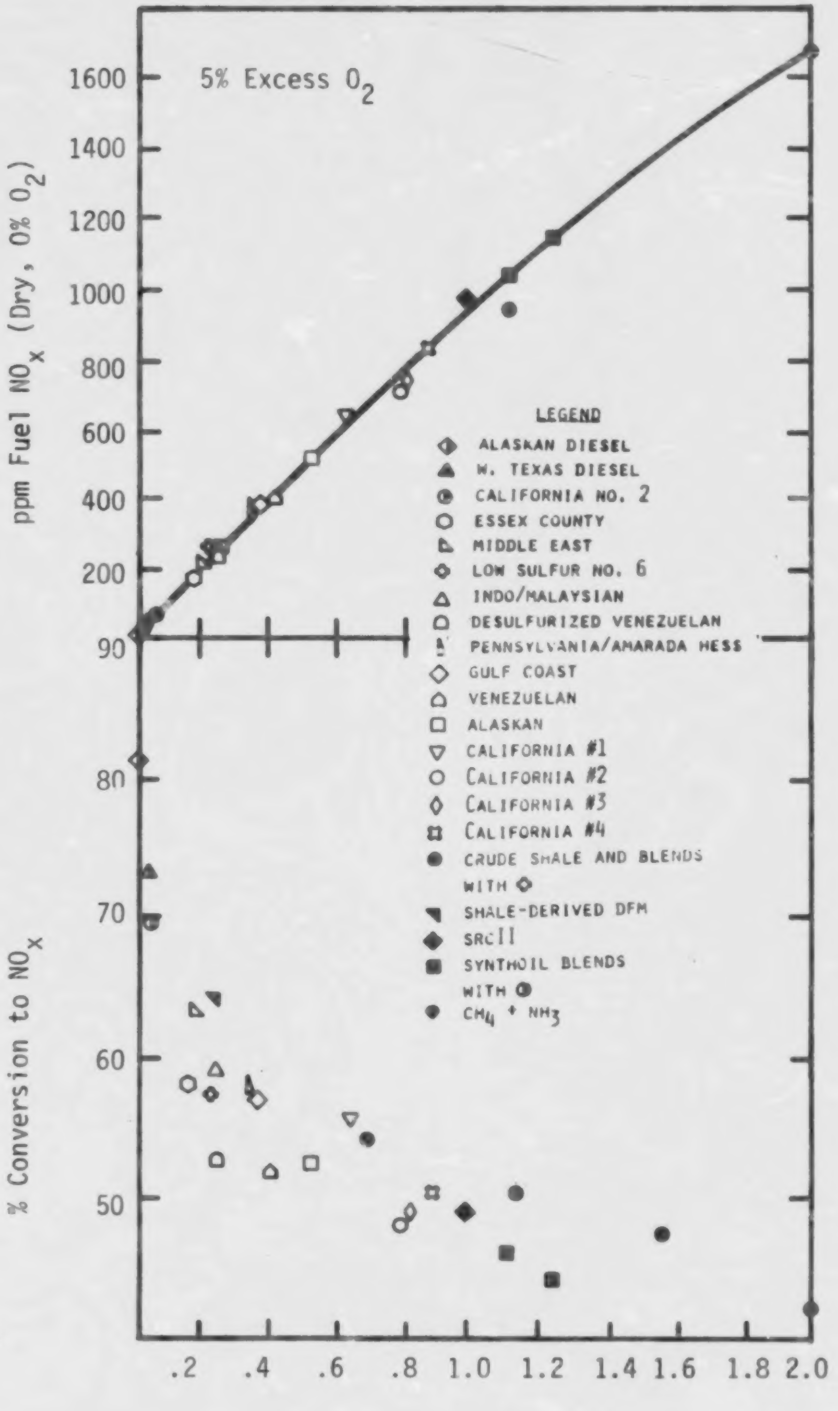


Figure 5. Fuel NO and Percent Conversion of Fuel Nitrogen to Fuel NO - LIquid Fuels, Ultrasonic Atomizer.

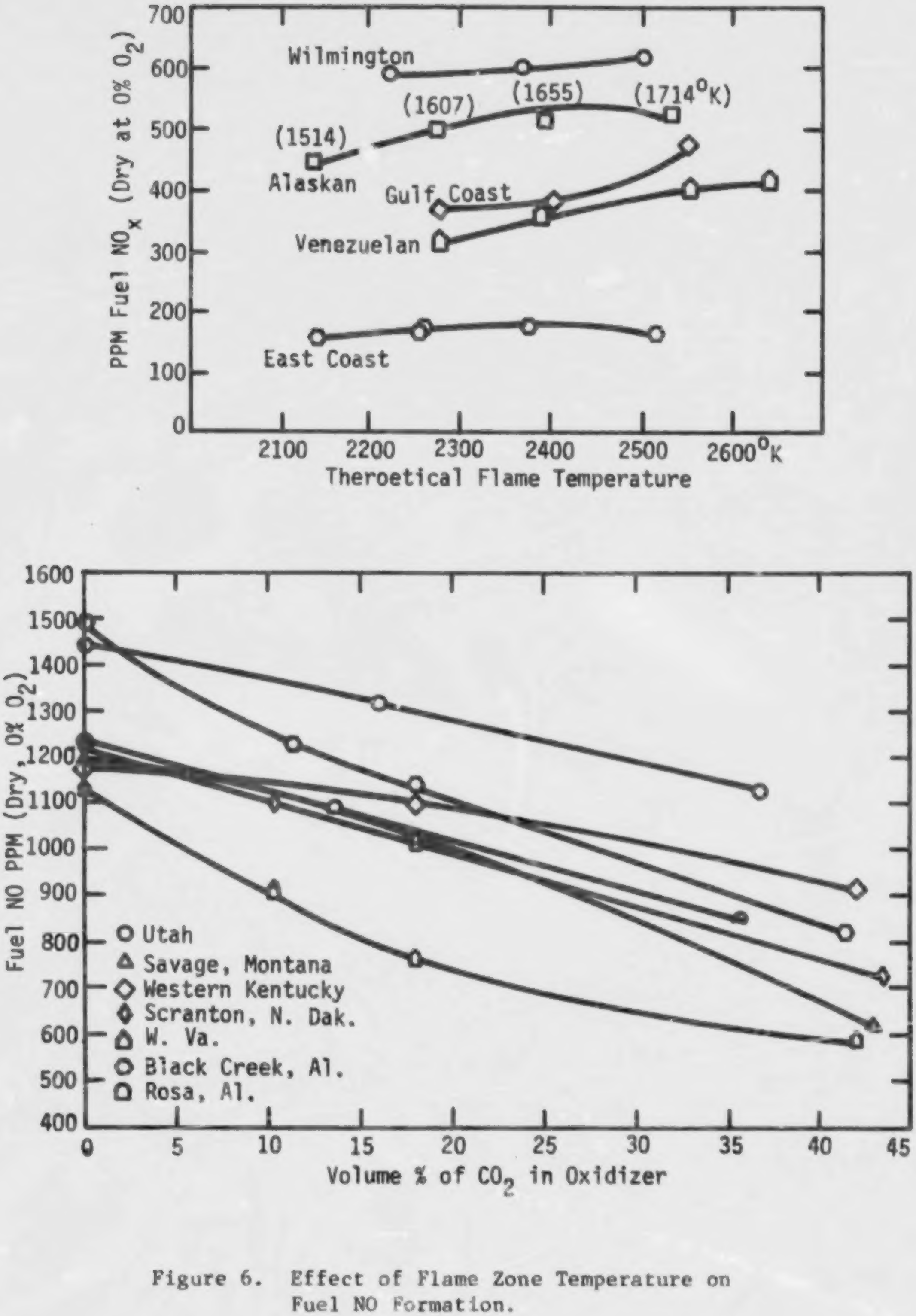


Figure 6. Effect of Flame Zone Temperature on Fuel NO Formation.

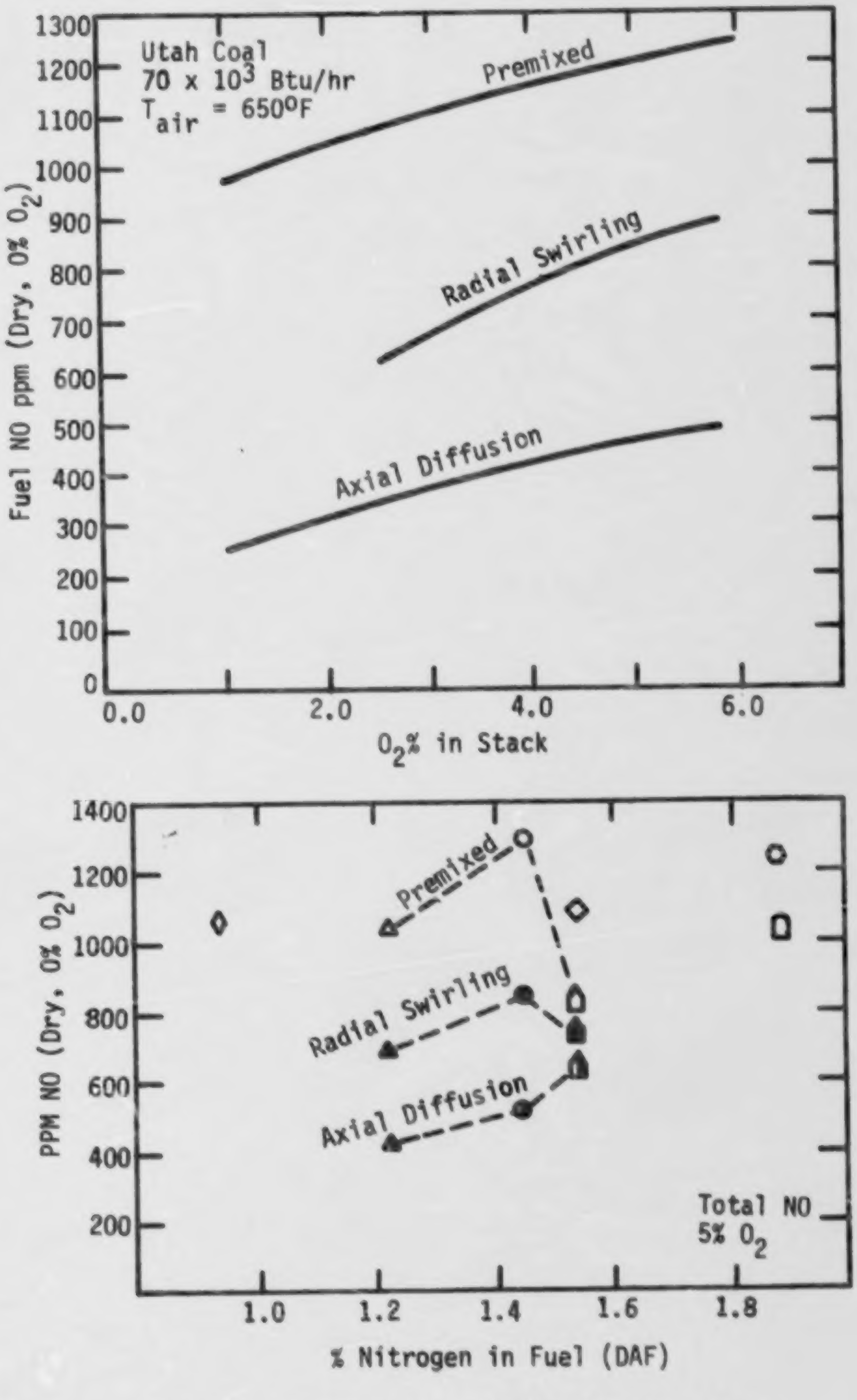


Figure 7. The Effect of Initial Fuel/Air Mixing - Coal.

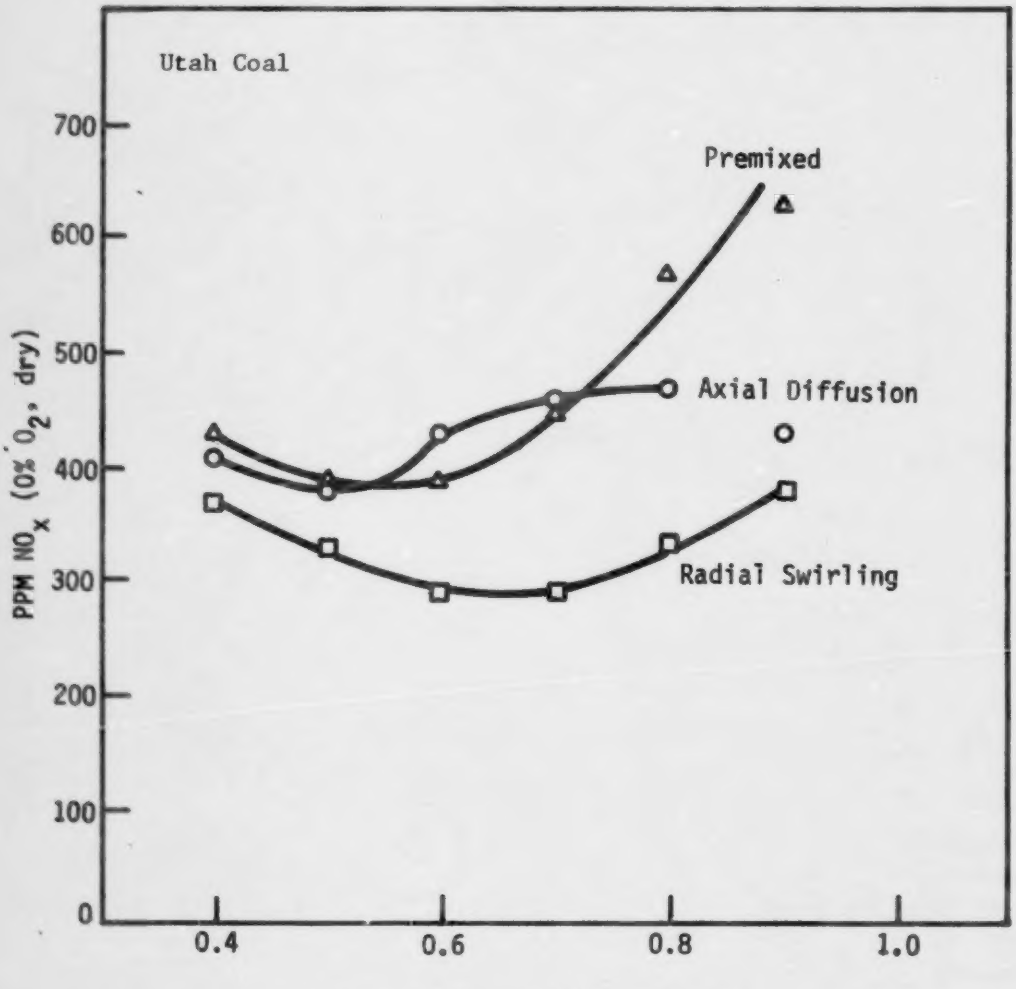


Figure 8. The Effect of Initial Fuel/Air Mixing - Staged, Coal.

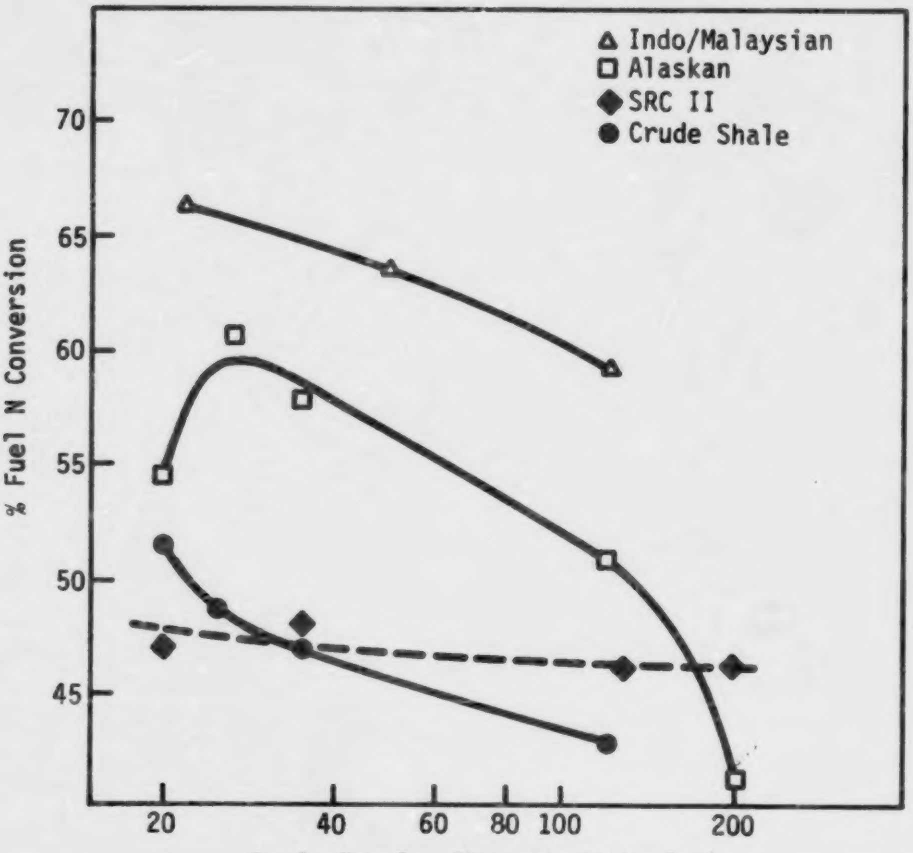


Figure 9. Effect of Droplet Size on Fuel Nitrogen Conversion.

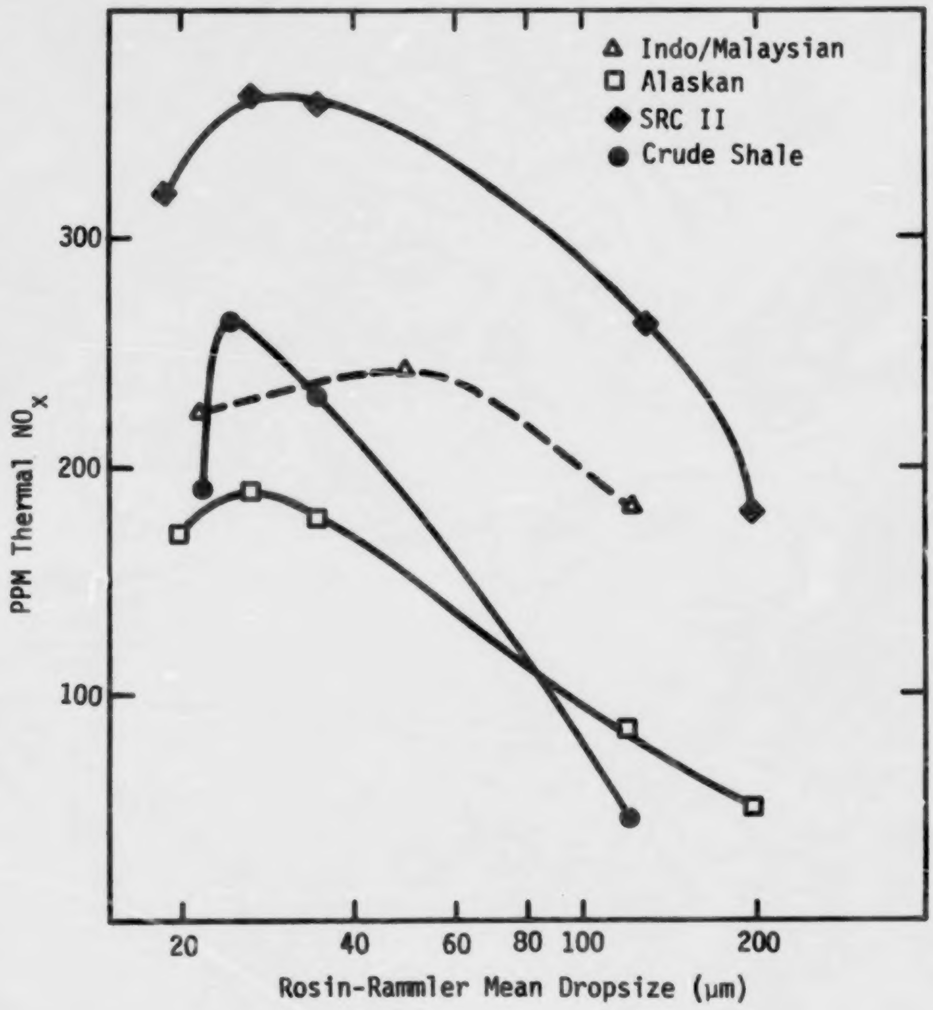
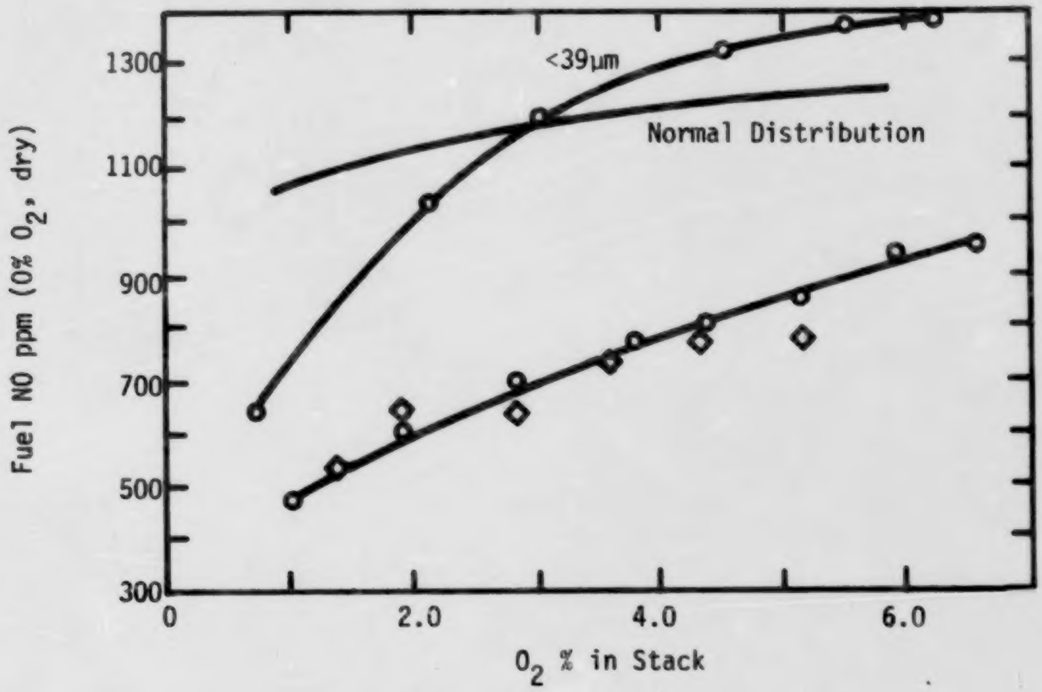
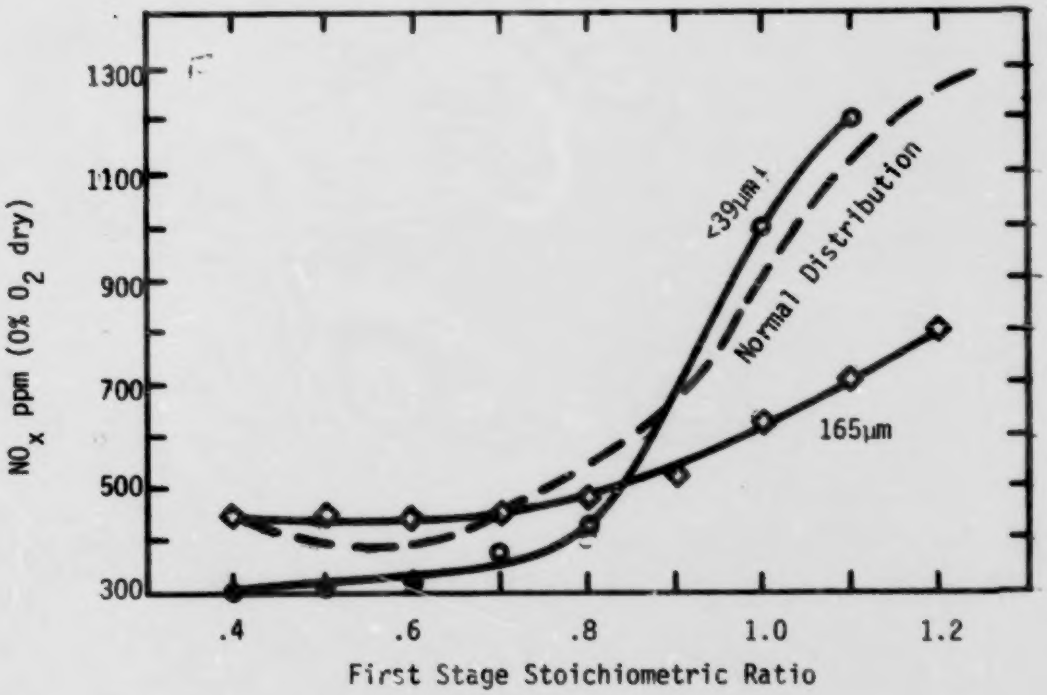


Figure 10. Effect of Droplet Size in Thermal NO_x Formation.



a) Premixed Unstaged



b) Staged

Figure 11. The Effect of Coal Particle Size on NO Formation.

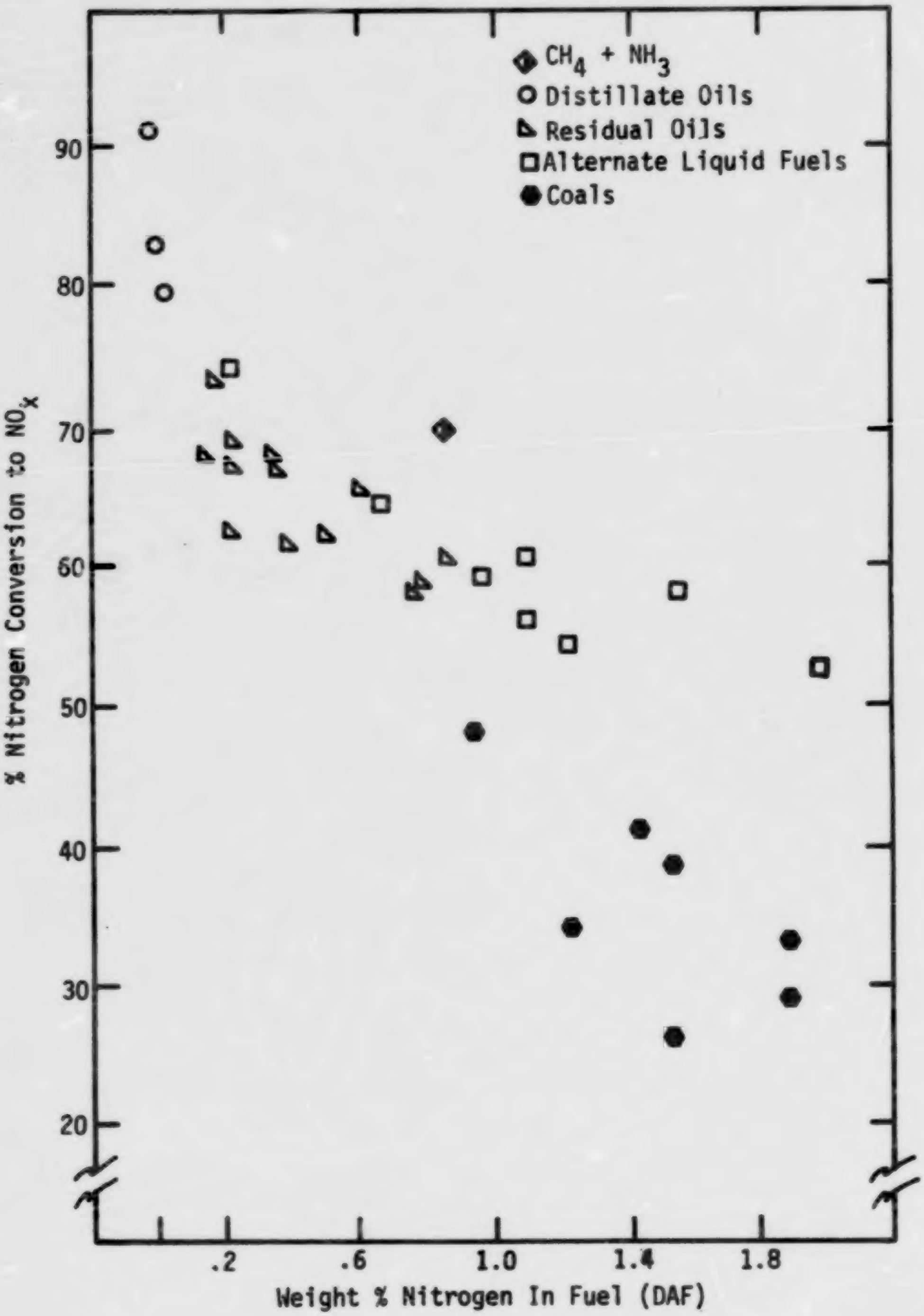


Figure 12. Overall Composite of Fuel Nitrogen Conversion - Unstaged.

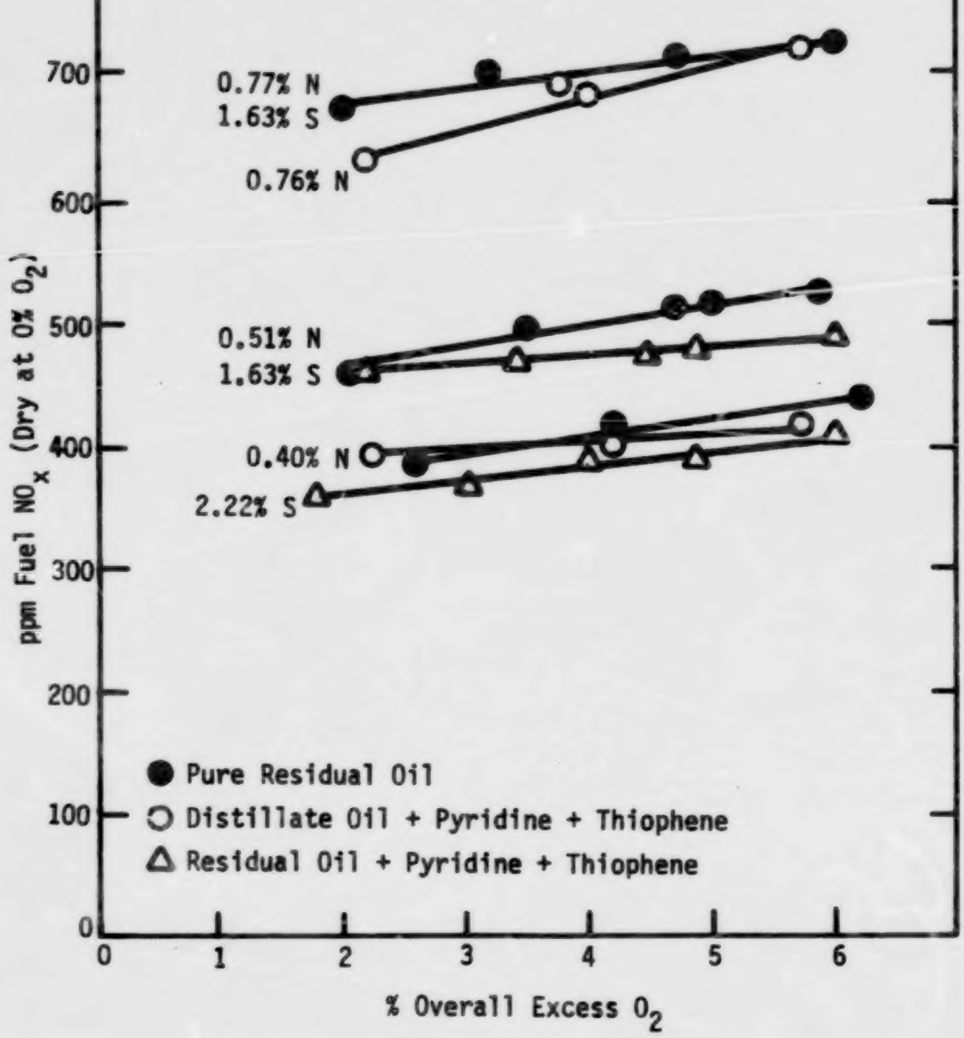


Figure 13. Relative Volatility Effects - Liquid Fuels - Unstaged.

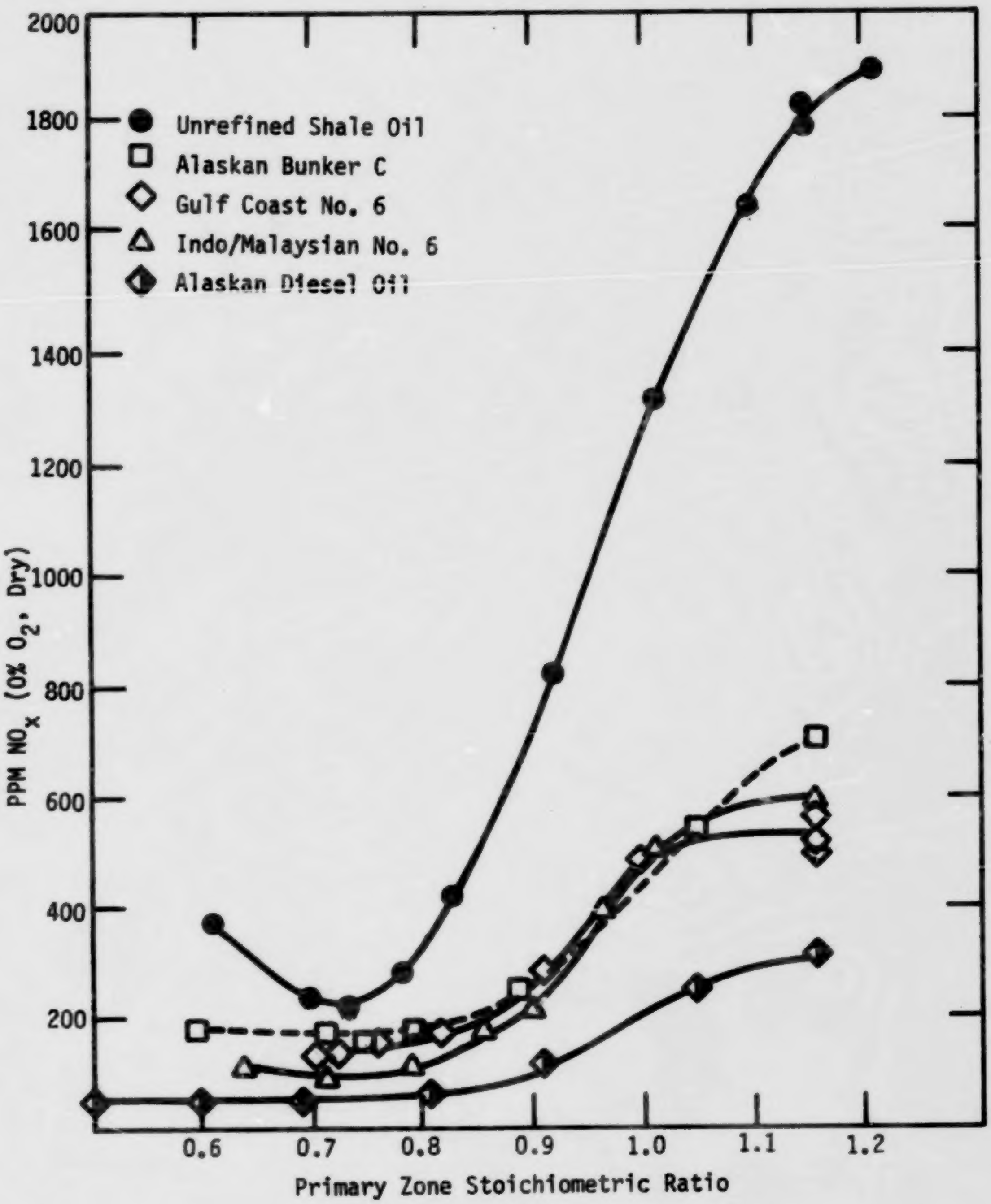


Figure 14. Effect of Liquid Fuel Composition on Emissions - Staged.

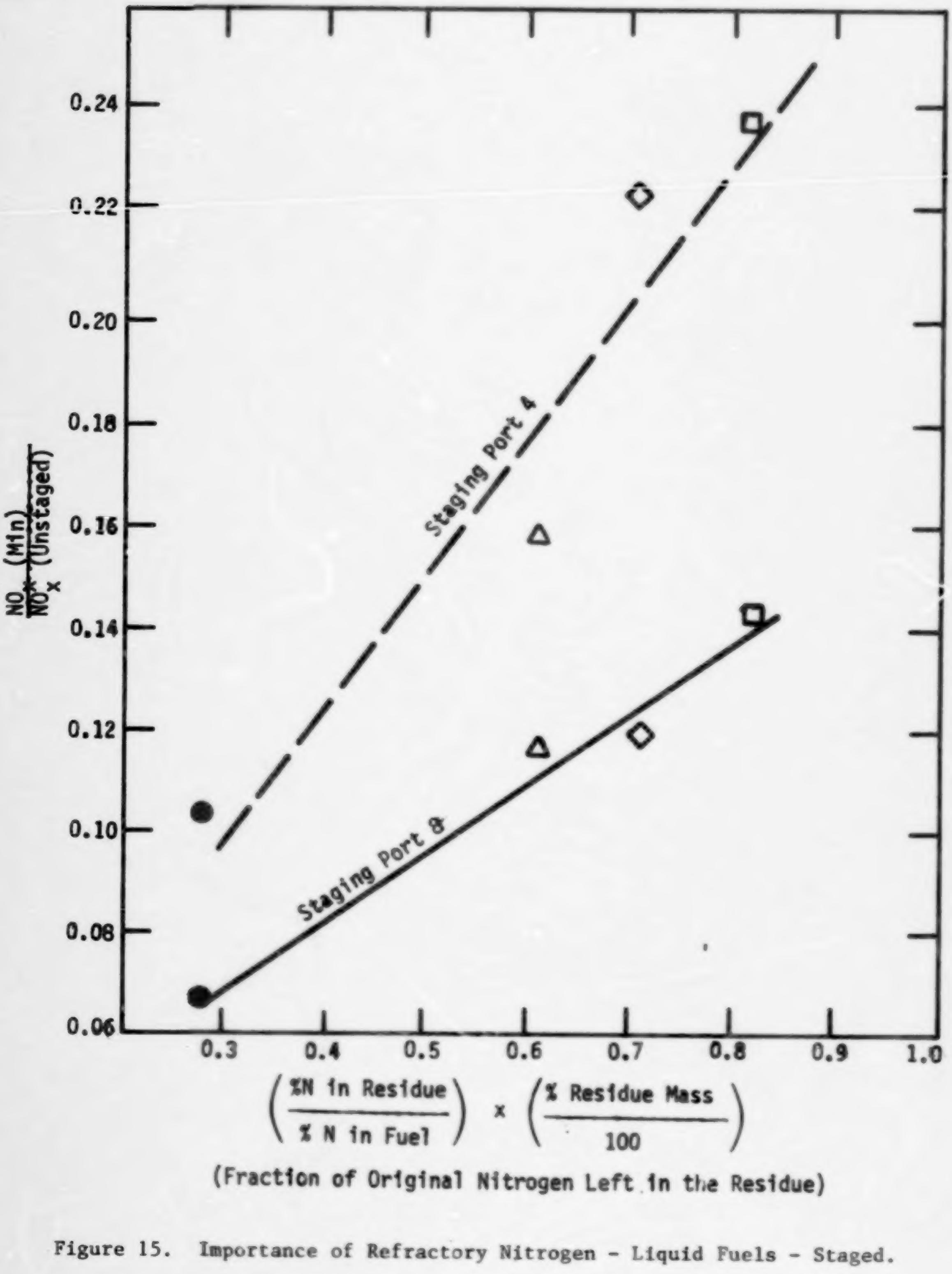


Figure 15. Importance of Refractory Nitrogen - Liquid Fuels - Staged.

TABLE I. LIQUID FUELS TESTED

	Alaskan Diesel	W. Texas Diesel	California Distillate	Essex County	Middle E. (Exxon)	Low S.* No. 6 Oil
Ultimate Analysis:						
Carbon, %	86.99	88.09	86.8	86.54	86.78	86.57
Hydrogen, %	12.07	9.76	12.52	12.31	11.95	12.52
Nitrogen, %	0.007	0.026	0.053	0.16	0.18	0.22
Sulfur, %	0.31	1.88	0.27	0.36	0.67	0.21
Ash, %	<.001	<.001	<.001	0.023	0.012	0.02
Oxygen, % (by difference)	0.62	0.24	0.36	0.61	0.41	0.46
Conradson Carbon Residue, %				2.1	6.0	4.4
Asphaltene, %				0.34	3.24	0.94
Flash Point, °F				205	350	325
Pour Point, °F				50	48	105
API Gravity at 60°F	33.1	18.3	32.6	24.9	19.8	25.1
Viscosity, SSU, at 140°F	33.0	32.0	30.8	131.2	490	222.4
at 210°F	29.5	28/8	29.5	45	131.8	69.6
Heat of Combustion:						
Gross Btu/lb			19,330	19,260	19,070	19,110
Net Btu/lb				18,140	17,980	17,970
Calcium, ppm				7.1	1.2	9.52
Iron, ppm				16	2.6	123.6
Manganese, ppm				0.09	0.02	0.46
Magnesium, ppm				3.7	0.08	2.23
Nickel, ppm				6.7	13	14.10
Sodium, ppm				37	0.98	3.74
Vanadium, ppm				14	25	3.11

TABLE I. LIQUID FUELS TESTED (CONTINUED)

	West Texas	Alaskan	California #1	California #2	California #3
Ultimate Analysis:					
Carbon, %	86.01	86.04	85.75	85.75	85.41
Hydrogen, %	9.72	11.18	11.83	11.44	11.23
Nitrogen, %	0.46	0.51	0.62	0.77	0.79
Sulfur, %	3.53	1.63	1.05	1.63	1.60
Ash, %	0.048	0.034	0.038	0.043	0.032
Oxygen, % (by difference)	0.23	0.61	0.71	0.71	1.02
Conradson Carbon Residue, %	20.08	12.9		8.72	9.22
Asphaltene, %	9.24	5.6		5.18	5.18
Flash Point, °F	205	215		--	150
Pour Point, °F	94	38		38	30
API Gravity at 60°F	6.2	15.6	19.5	15.4	15.1
Viscosity, SSU, at 140°F	29,720	1,071	246.1	854	748.0
at 210°F	1,824	194	70.00	129	131.6
Heat of Combustion:					
Gross Btu/lb	17,800	18,470	--	18,470	18,460
Net Btu/lb	16,910	17,580		17,430	17,440
Calcium, ppm	5.9	6.9		21	14
Iron, ppm	43	24		73	53
Manganese, ppm	0.13	0.06		0.8	0.1
Magnesium, ppm	0.9	1.4		5.1	3.8
Nickel, ppm	29	50		65	82
Sodium, ppm	3.2	37		21	2.6
Vanadium, ppm	60	67		44	53

TABLE I. LIQUID FUELS TESTED (CONTINUED)

	Indo Malaysian	Venezuelan Desulphurized	DFM (Shale)	Pennsylvania (Amarada Hess)	Gulf Coast
Ultimate Analysis:					
Carbon, %	86.53	85.92	86.18	84.82	84.62
Hydrogen, %	11.93	12.05	13.00	11.21	10.77
Nitrogen, %	0.24	0.24	0.24	0.34	0.36
Sulfur, %	0.22	0.93	0.51	2.26	2.44
Ash, %	0.036	0.033	0.003	0.067	0.027
Oxygen, % (by difference)	1.04	0.83	1.07	1.3	1.78
Conradson Carbon, Residue %	3.98	5.1	4.1	12.4	14.8
Asphaltene, %	0.74	2.59	0.036	4.04	7.02
Flash Point, °F	210	176	182	275	155
Pour Point, °F	61	48	40	66	40
API Gravity at 60°F	21.8	23.3	33.1	15.4	13.2
Viscosity, SSU, at 140°F	199	113.2	36.1	1049	835
at 210°F	65	50.5	30.7	240	181
Heat of Combustion:					
Gross Btu/lb	19,070	18,400	19,430	18,520	18,240
Net Btu/lb	17,980	17,300	18,240	17,500	17,260
Calcium, ppm	14	8.7	0.13	9.2	4.4
Iron, ppm	16	6.5	6.3	13.2	19
Manganese, ppm	0.13	0.09	0.06	0.10	0.13
Magnesium, ppm	3.6	3.6		3.3	0.4
Nickel, ppm	19	19	0.43	32.7	29
Sodium, ppm	15	15	0.09	64.5	3.6
Vanadium, ppm	101	101	<.1	81.5	45

TABLE I. LIQUID FUELS TESTED (CONTINUED)

	California #4	Synthoil	Shale (Crude)
Ultimate Analysis:			
Carbon, %	86.66	86.30	84.6
Hydrogen, %	10.44	7.44	11.3
Nitrogen, %	0.86	1.36	2.08
Sulfur, %	0.99	0.80	0.63
Ash, %	0.20	1.56	.026
Oxygen, % (by difference)	0.85	2.54	1.36
Conradson Carbon, Residue %	15.2	23.9	2.9
Asphaltene, %	8.62	16.55	1.33
Flash Point, °F	180	210	250
Pour Point, °F	42	80	80
API Gravity at 60°F	12.6	S=1.14	20.3
Viscosity, SSU, at 140°F	720	10,880	97
at 210°F	200	575	44.1
Heat of Combustion:			
Gross Btu/lb	18,230	16,480	18,290
Net Btu/lb	17,280	15,800	17,260
Calcium, ppm	90.6	1,670	1.5
Iron, ppm	77.2	109	47.9
Manganese, ppm	0.87	6.2	0.17
Magnesium, ppm	31.4	170	5.40
Nickel, ppm	88.0	2.6	5.00
Sodium, ppm	22.3	148	11.71
Vanadium, ppm	66.2	6.5	<.3

TABLE II. SOLID FUELS INVESTIGATED

EER COAL DESIGNATION	B	D	4	11	18	19	20
Coal Source	West Virginia	Utah	Scranton N.D.	Montana Savage #11	Rosa Alabama	Black Creek Alabama	Western KY
Ultimate Analysis:							
Carbon, %	71.57	68.49	42.02	41.36	74.72	80.27	69.50
Hydrogen, %	4.94	5.20	2.71	2.57	4.36	5.09	4.76
Nitrogen, %	1.33	1.24	0.54	0.72	1.60	1.75	1.33
Sulfur, %	1.09	0.64	0.99	0.27	0.96	0.74	2.95
Ash, %	11.66	7.40	7.50	4.61	6.79	4.45	7.81
Oxygen, % (by difference)	7.54	10.64	11.28	14.11	3.55	5.45	8.85
Proximate Analysis:							
Moisture, %	1.87	6.39	34.96	36.36	8.02	2.25	4.80
Volatiles, %	32.53	38.89	28.85	--	21.81	28.28	36.10
Ash, %	11.66	7.40	7.50	4.61	6.79	4.45	7.80
Fixed Carbon, %	53.94	47.32	28.69	--	63.38	65.02	51.1
Calorific Value (Btu/lb)		12,340	6,446	6,995	13,394	14,284	12,450
Forms of Sulfur							
Pyritic, %			0.32	0.01	0.43	0.07	
Organic, %			0.65	0.26	0.47	0.67	
Sulfate, %			0.02	0.00	0.06	0.00	

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THE CONTROL OF POLLUTANT FORMATION IN FUEL OIL FLAMES — THE INFLUENCE OF OIL PROPERTIES AND SPRAY CHARACTERISTICS

By:

G. C. England, M. P. Heap, R. T. Horton, D. W. Pershing and G. Flament*
Energy and Environmental Research Corporation
Irvine, California 92715

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*International Flame Research Foundation, IJmuiden, Holland

ABSTRACT

Pollutant production in liquid fuel flames is controlled by the complex interaction of the liquid fuel spray and the combustion air flow field. This paper presents results of a study to investigate the influence of atomizer design and fuel properties under both normal and staged combustion conditions on nitrogen oxide formation. The sprays produced from the various atomizers were characterized under isothermal conditions by a method involving the diffraction of laser light.

ACKNOWLEDGEMENTS

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SECTION 1

INTRODUCTION

Although the increased utilization of coal provides a partial solution to the U. S. energy crisis, a balanced fuel economy necessitates that in the future many industrial users will burn petroleum, coal or shale-derived residual fuels. The relatively high nitrogen content and low hydrogen-to-carbon ratios associated with these liquid fuels suggests that their use may be accompanied by an increase in two pollutants unless preventive measures are taken. The production of nitrogen oxides (NO_x) and particulate matter from a given fuel in turbulent diffusion flames is controlled by the fuel/air contacting process, which is dependent upon the complex interaction of the liquid fuel spray and the combustion air flow field. A major fraction of the nitrogen oxides produced in residual fuel oil flames is formed by the oxidation of nitrogen contained in the fuel. The fraction of fuel nitrogen which is converted to fuel NO is almost completely dependent upon the oxygen availability during the thermal decomposition of the liquid droplets. Particulate matter produced in residual fuel oil flames consists of soot, which is produced from the gas phase specie, and two other constituents, cenospheres and coke, production of which is associated with the multi-component nature of the fuel and the characteristics of droplet combustion. The formation of these latter two components can be attributed to the occurrence of liquid phase thermal cracking because of high droplet temperatures. Soot formation, which occurs in three distinct phases: nucleation, surface growth, and coagulation, is associated with the existence of fuel-rich zones within the flame. Thus, local stoichiometry which is controlled by the turbulent mixing process and is spray/flow field-dependent plays a dominant role in the formation of NO_x and particulate matter.

Bench-scale studies (1) indicate that the total nitrogen content of liquid fuels is the major parameter controlling fuel NO formation under overall fuel-lean conditions. The fuel nitrogen speciation appears to be a secondary parameter unless the fuel is being burned under staged combustion conditions, when fuel nitrogen volatility appears to limit NO_x reduction achievable under staged combustion. Field studies (2) have investigated the influence of fuel properties and atomizer design on both the pollutant emissions from, and thermal efficiency of operating boilers. Although these studies indicated that both of these parameters were important, the nature of the tests precluded the identification of the controlling parameters. The results presented in this paper were obtained under conditions which were typical of industrial practice, and yet allowed the influence of atomizer type and fuel properties to be identified under comparable conditions. The specific objectives of the research program were:

- To relate the formation of nitrogen oxides in liquid fuel flames to atomizer design and to fuel oil properties.
- To investigate the interaction between liquid sprays and the airflow pattern for conditions typical of package boilers under normal and staged conditions.

The information generated by this program will provide for the generalization of low-NO_x oil burner technology for application to package boilers.

SECTION 2

EXPERIMENTAL SYSTEMS

The combustion experiments were conducted in an axisymmetric combustor at a nominal firing rate of 3×10^6 Btu/hr. (.88 MW). This combustor, which has been described in detail elsewhere (3), allowed the addition of cooled combustion products to the combustion air supply and had the capability of dividing the combustion air into two separate streams to allow operation under staged combustion conditions. In these investigations the staged air was injected through an axial boom inserted from the rear of the combustion chamber. The distance of the air injector from the fuel atomizer could be varied. Standard techniques and instrumentation were employed for the measurement of flue gas composition.

BURNER AND ATOMIZERS

The commercial burners used in this investigation were fitted to an axial oil gun in a simple burner system which consisted of:

- a refractory divergent exit, 45° half angle
- an annular air duct with interchangeable fixed-vane swirlers generating an axial velocity of 100 ft/sec (31 m/sec) and swirl numbers of 0.21, .45 and .79.

The oil gun was precisely positioned to locate all the atomizers at the throat of the divergent and the combustion air supply was designed to give a uniform air distribution across the throat. A steam/auxiliary electric heating system was used to maintain the oil temperature (measured by a thermocouple) at the oil nozzle constant. Table 1 lists the atomizers used in the study which were of the twin fluid (air or steam assist) type.

SPRAY CHARACTERIZATION

The characteristics of the sprays produced by the commercial atomizers used in the study were not available at the time this paper was written.

Droplet size distribution will be determined under quiescent isothermal conditions using a laser droplet size analyzer based on the Fraunhofer Diffraction pattern of a laser beam by the particles moving through a cross-section of the beam (4). The particle cloud of a spray causes a deflection of a portion of the parallel beam giving a conical pattern of diffracted light. There is a direct relationship between the diameter of the particle (assumed spherical) and the angle of the light diffracted by this particle. Therefore, it is possible to calculate the particle size distribution of a cloud of particles by an evaluation of the diffracted light energy. The conical diffracted light pattern is measured in the focal plane of a lens by a photo detector element composed of 30 annular rings whose radii increase from 0.148 mm to 14.56 mm. The instrument evaluates the drop-size distribution and expresses it in a Rosin-Rammler form together with the weight percentage and number of drops in each of 15 groups.

The advantages of this laser diffraction technique are that it is fast in comparison to photographic techniques, requires no calibration for particles with diameters ranging from 10 to 500 μm and it does not interfere with the spray. However, there may well be major limitations associated with the use of this technique and a comparison of various optical techniques for spray characterization has been initiated under the FCR program. The primary limitation of the diffraction technique is that imposed by spray density which arises due to multiple scattering. Other limitations include an undefined influence of droplet velocity, a minimum drop size detectability of 10 μm and the use of the Rosin-Rammler distribution.

Figure 1 provides an illustration of the use of this instrument to compare drop-size distribution from three atomizers:

- a pressure jet (mechanical)
- a single lobe of a Y-jet (twin fluid)
- an ultrasonic atomizer (twin fluid)

It can be seen that the pressure jet and the Y-jet give very similar drop-size distributions while the ultrasonic atomizer gives small droplets with a narrow size distribution around 20 μm.

FUELS

The fuels used during the investigation are listed in Table II, together with selected properties. Figure 2 presents the results of a Differential Thermal Analysis (DTA) and Figure 3 shows the mass evolution of nitrogen as a function of distillation temperature. The DTA clearly shows the multi-component nature of the petroleum-derived residual fuels. It can also be seen that the nitrogen in the shale-derived fuels (Nos. 4 and 8) is evolved at a much lower temperature than that from petroleum-based residual fuels. Apparently the nitrogen species in the Gulf Coast and North Slope oils (Nos. 5 and 6) appear to be refractory in nature since almost all the nitrogen remains in the residuum.

SECTION 3

RESULTS

The series of investigations planned to define the influence of atomizer design and fuel characteristics on the emission of NO_x from residual fuel oil-fired flames can most conveniently be described under two separate headings: those concerned with normal excess air conditions, and those which pertain to two-stage combustion in which the first stage was operated fuel-rich and air was added to the rich combustion products downstream from the fuel nozzle to complete combustion.

NORMAL EXCESS AIR CONDITIONS

The results presented in Figure 4 compare NO_x emissions as a function of overall excess air level for a single fuel (No. 3) with a burner swirl number of 0.45. It can be seen that in general the NO_x emissions increase with increasing excess air level for each atomizer. However, there is a wide range in emission level for different atomizers. The results presented in Figure 5 show the influence of fuel type on NO_x emissions at two swirl levels, $S = 0.45$ and 0.79, with a single nozzle (B). These results clearly show the impact of the flow field on NO_x formation.

It is generally recognized that NO_x emissions increase with increasing fuel nitrogen content. Figure 6 presents a plot of NO_x emissions as a function of fuel nitrogen content for four different atomizers and two swirl levels. For each atomizer there appears to be an almost linear relationship between NO_x emission and fuel nitrogen content. However, this relationship is not general and depends both upon atomizer design and the flow field conditions. For instance, atomizer B gave very high NO_x emissions which were similar to those produced by atomizer A at the low swirl level. However, at the higher swirl condition emissions from atomizer A were almost unaffected by the swirl level, whereas those from atomizer B were considerably reduced. At the intermediate swirl level the four atomizers appear to fall into two categories, whereas at the high swirl level three of the four atomizers behaved similarly.

The data presented in Figure 6 illustrates some of the difficulties associated with any general correlation relating fuel nitrogen content to emissions since the nature of the combustion system has a significant influence.

STAGED COMBUSTION CONDITIONS

Staged combustion, i.e., the operation of a combustion system in which the fuel originally burns under oxygen-deficient conditions, provides the most cost-effective control technique for reducing fuel NO. The results presented in Figure 7 show the influence of atomizer design on the emission of NO_x at an overall excess air level corresponding to three percent excess oxygen as a function of the percentage of theoretical air in the fuel-rich primary zone. The burner throat conditions were unmodified, and therefore, as the percentage of theoretical air in the primary zone decreases, the burner throat velocity also decreases. The second stage air was added at the same location for each atomizer. The atomizer design has a significant influence upon the minimum NO_x achieved under staged combustion conditions. All of the nozzles show the same characteristic performance. As the primary zone becomes more fuel-rich NO_x emissions decrease to a minimum and then increase. This increase is probably associated with the escape of fuel nitrogen specie from the primary zone where they are oxidized to NO when the second staged air is added. Comparing the minimum emission levels with those reported for the bench-scale furnace with the same fuels, it can be seen that the results shown in Figure 7 do not show the same degree of control. This can be attributed to two factors. The bench-scale combustor has refractory walls, and therefore the initial fuel rich stage will be at a higher temperature. Residence times in the bench-scale combustor rich zone were also much longer than those achieved in the cold-wall combustor.

The trade-off between the decrease in NO_x emissions and the increase in smoke emissions is illustrated by the data presented in Figure 8 which shows NO_x and Bacharach smoke number as a function of percent theoretical air in the primary zone for three swirl conditions with a single nozzle. The NO_x emissions appear to be relatively insensitive to primary zone swirl number for this particular nozzle. However, it can be seen that the smoke emissions differ considerably for the same range of swirl levels.

A cylindrical refractory extension 36 inches (.91 meter) long was added to the divergent burner exit to ascertain whether the reduced heat loss in the first stage could account for the different emission levels achieved in the combustor and the bench-scale experiments. The addition of this refractory extension had almost no effect upon exhaust NO_x emissions.

Figures 9 and 10 present data comparing the performance of two atomizers under staged combustion conditions for two different fuels and zero swirl in the primary zone. One fuel was essentially free from nitrogen, and it can be seen that the emission levels from the two nozzles are dependent upon fuel nitrogen content. Also, at low theoretical air ratios in the primary zone nozzle A gives higher smoke emissions than nozzle B for both fuels.

SECTION 4

DISCUSSION

Data available from both field and development studies indicates that the emission of nitrogen oxides from cold-wall combustors is a complex function of fluid dynamics and fuel chemistry. The results presented in this paper were part of an investigation planned to provide data under well-controlled conditions to define the effect of fuel properties and atomizer parameters on pollutant emissions from combustion systems typical of those encountered in practice. At the time of writing the paper one section of the investigation, that concerned with spray characterization, had not been completed, and therefore the interpretation of the results can only be considered as preliminary.

The primary fuel parameter controlling NO_x formation in liquid fuel flames is the fuel nitrogen content of the oil. NO_x emissions increase with increasing nitrogen content. However, the conversion of fuel nitrogen to NO_x is strongly dependent upon the mixing of fuel and air within the flame. This interaction is illustrated by the results presented in Figure 11 which shows the NO_x emissions as a function of fuel nitrogen content obtained with atomizer B. The open data symbols refer to measurements made with pure combustion air. The partially shaded data symbols refer to NO_x emissions measured when the combustion air was vitiated with approximately 20 percent flue gas recirculation. It can be seen that with flue gas recirculation emissions are almost independent of swirl level and very similar to those obtained with unvitiated air at a swirl level of $S = 0.79$. This could be interpreted as meaning that the difference in emission levels between the two swirl levels is due to thermal NO production. However, this is probably an erroneous conclusion since the addition of flue gas recirculation will not only lower flame temperatures due to the addition of an inert thermal ballast but will also modify the mixing process due to the increased throat velocities. Extrapolation of the two unvitiated lines to zero percent nitrogen indicates a thermal NO_x production of approximately 170 ppm which is higher than that achieved with low nitrogen diesel fuels. Figure 11 also allows a comparison between the bench-scale results (1) and those obtained in this investigation. The thermal characteristics of the bench-scale furnace are different from the 3,000,000 Btu/hr combustor, and therefore, only the fuel NO_x emissions have been plotted. The same atomizer design was used for both investigations, although the capacity was different. Apparently fuel nitrogen conversions were higher in the bench-scale investigations than those obtained in the combustor. This might well be associated with a change in drop size as the atomizer capacity is increased, i.e., for a given atomizer design drop size is not independent of capacity.

The influence of atomizer design on NO_x emissions is probably due to the combined effect of drop-size distribution, spray pattern, and the momentum of the droplets. Since these parameters will control the heating rate, penetration of the droplets through recirculation zones and the local stoichiometry. Figure 12 compares the performance of five nozzles with a single fuel as a function of swirl level. As the swirl level increases the size and intensity of the internal axial recirculation zone will increase, and the NO_x emissions are for the most part, associated with the interaction of the spray and the internal recirculation zone. It appears that different nozzle designs will influence this interaction. For example, nozzle A shows a continual decrease of emissions with increasing swirl level, whereas many of the other nozzles show a minimum emission at the intermediate swirl level. Table III presents the ratio of NO_x at swirl level equal to 0.5 and 0.79 for four atomizers and four fuels. This table indicates that there is also an influence of fuel properties on the interaction of the spray and the flow field since for a given atomizer increasing the swirl level may increase or decrease the nitrogen oxide emission.

It was noted earlier that the NO_x reductions achieved in the bench-scale experiments were higher than those obtained in the combustor. This can be seen in Figure 13, which compares the emissions from a staged crude shale oil containing over 2 percent nitrogen. In the bench-scale studies at the shortest primary zone residence time of 400 msec minimum emissions were approximately

200 ppm. In the combustor primary zone residence time was much shorter, about 200 msec, and emissions were always greater than 300 ppm.

It can be seen that there is a very significant effect of atomizer design upon NO_x emissions. The atomizer giving the lowest emissions under staged conditions gave the highest value unstaged. Comparison with information presented by Heap et al (1) would suggest that nozzle B has a much smaller drop-size distribution than nozzle A, thus allowing for more rapid vaporization of the fuel nitrogen compounds in the primary zone giving more time for the formation of N_2, and thus, lower overall emissions.

REFERENCES

1. Heap, M. P., D. W. Pershing, G. C. England, J. W. Lee, and S. L. Chen. The Influence of Fuel Characteristics on Nitrogen Oxide Formation - Bench-Scale Studies. Third Symposium on Stationary Source Combustion, March 1979.

2. Cato, G. A., L. J. Muzio, and P. E. Shore. Field Testing: Application of Combustion Modification to Control Pollutant Emissions from Industrial Boilers, Phase II. EPA Report No. 600/1-76-086a, April 1976.

3. Muzio, L. J., and R. P. Wilson. Experimental Combustor for Development of Package Boiler Emission Control Techniques. Phase I of III, EPA-R2-73-292a (NTIS PB No. 224274/AS), July 1973.

4. Swithenbank, J., J. M. Beer, D. S. Taylor, D. Abbott, and G. C. McCreath. A Laser Diagnostic for the Measurement of Droplet and Particulate Size Distribution. University of Sheffield, Department of Chemical Engineering and Fuel Technology. Report 1976.

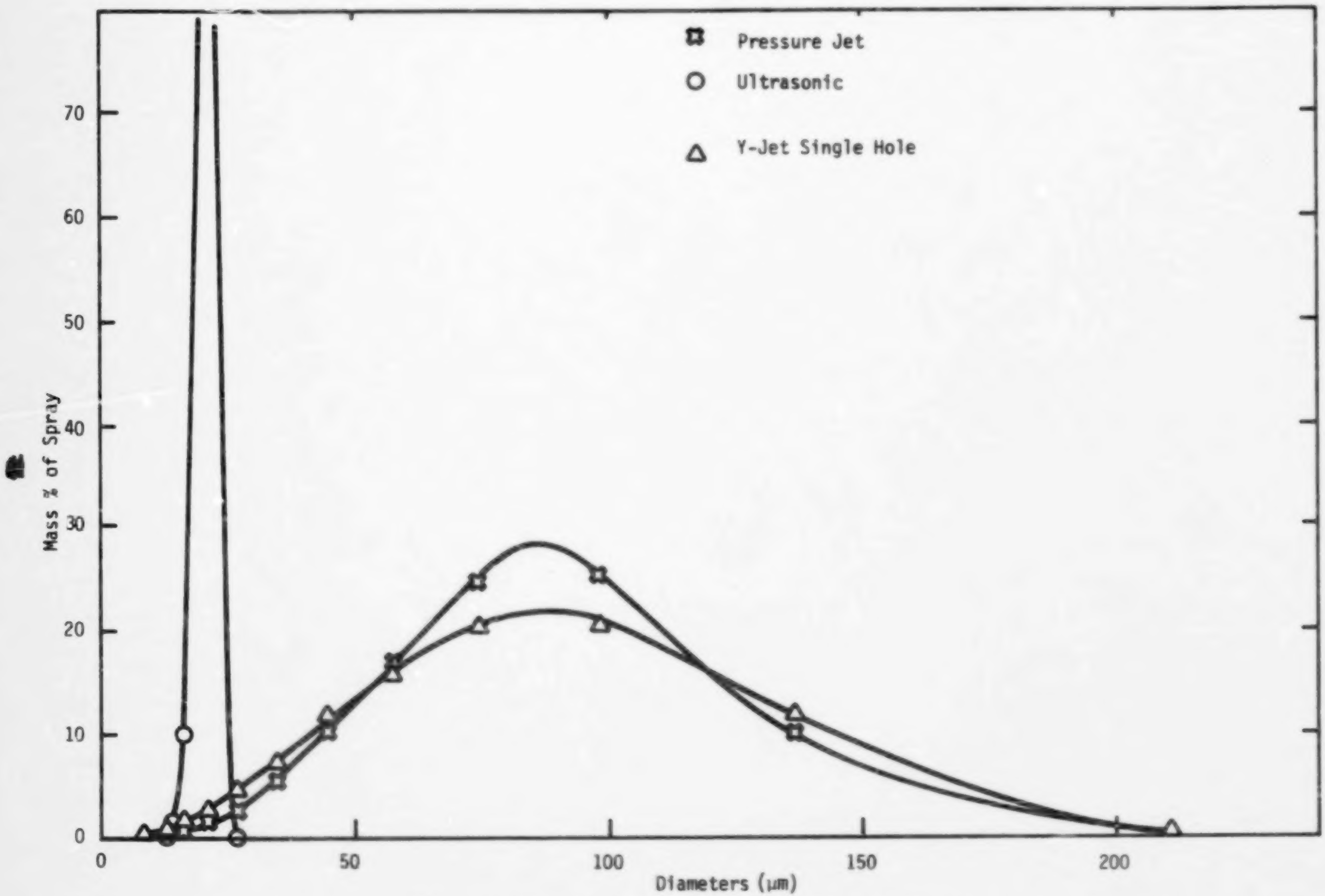


Figure 1. Dropsize Distribution for Three Atomizers.

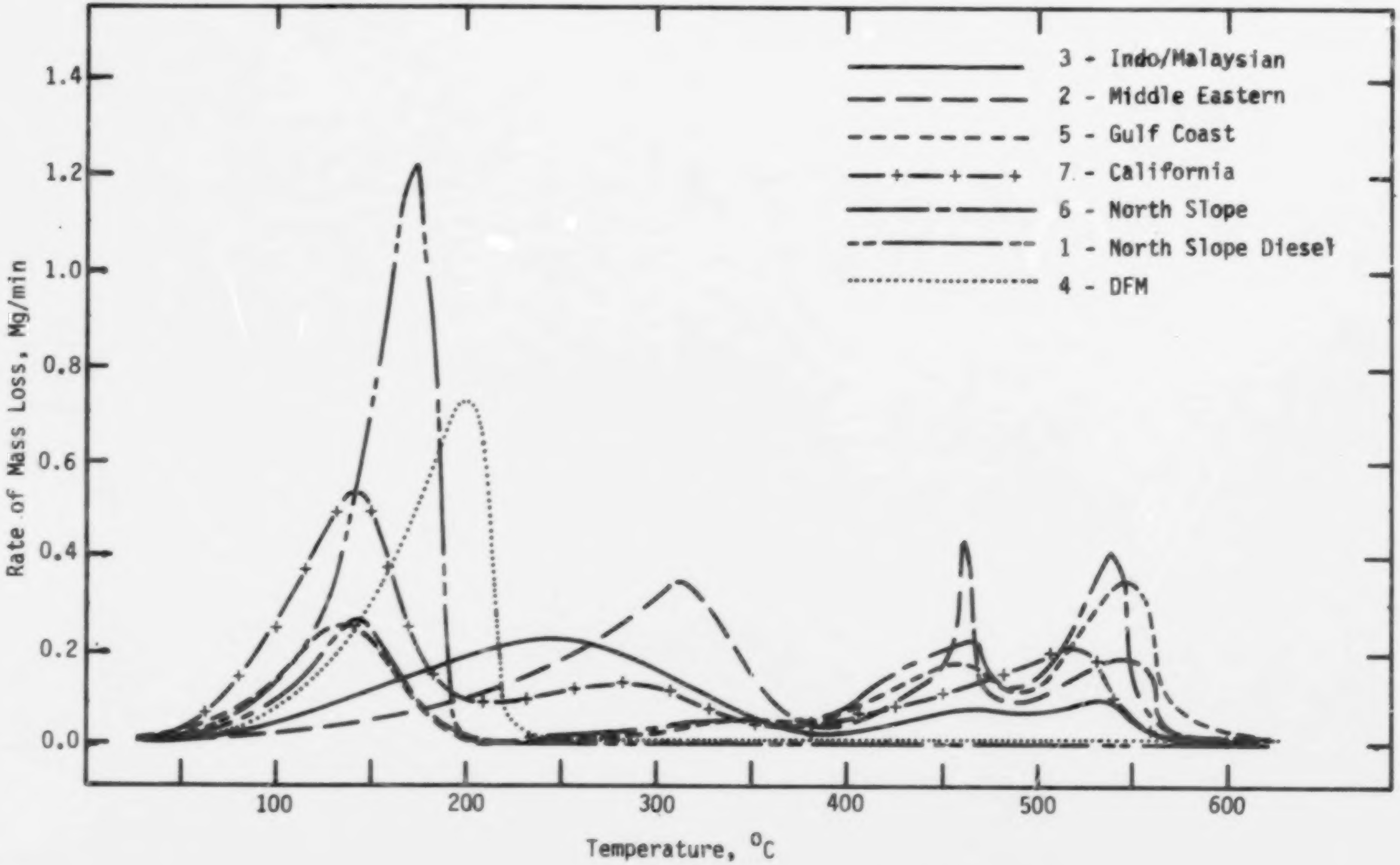


Figure 2. DTA Analysis of Eight Fuel Oils.

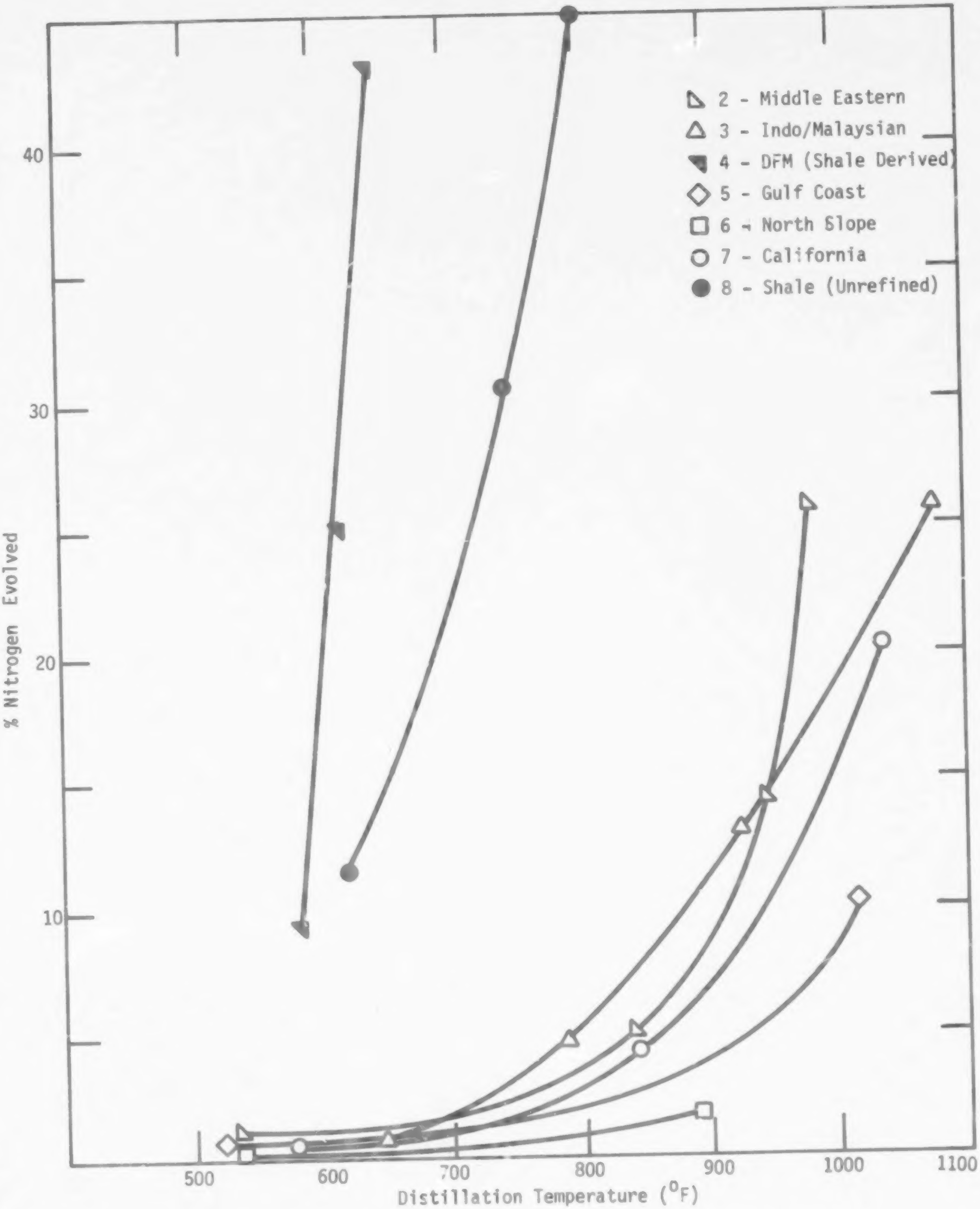


Figure 3. Vacuum Distallation Results - Nitrogen Evolution.

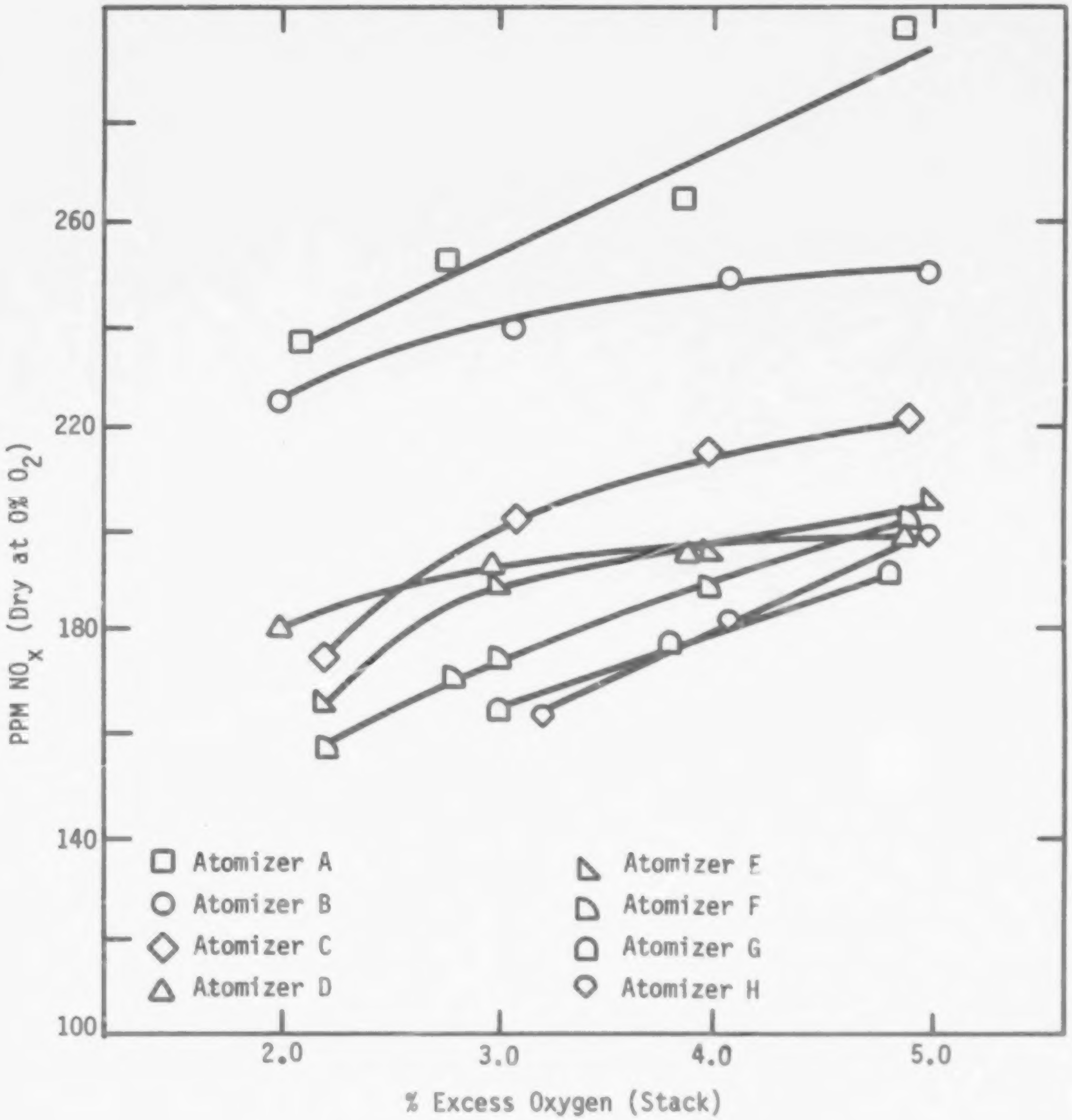


Figure 4. Comparison of NO_x Emissions for Eight Commercial Atomizers in a Common Flow Field.

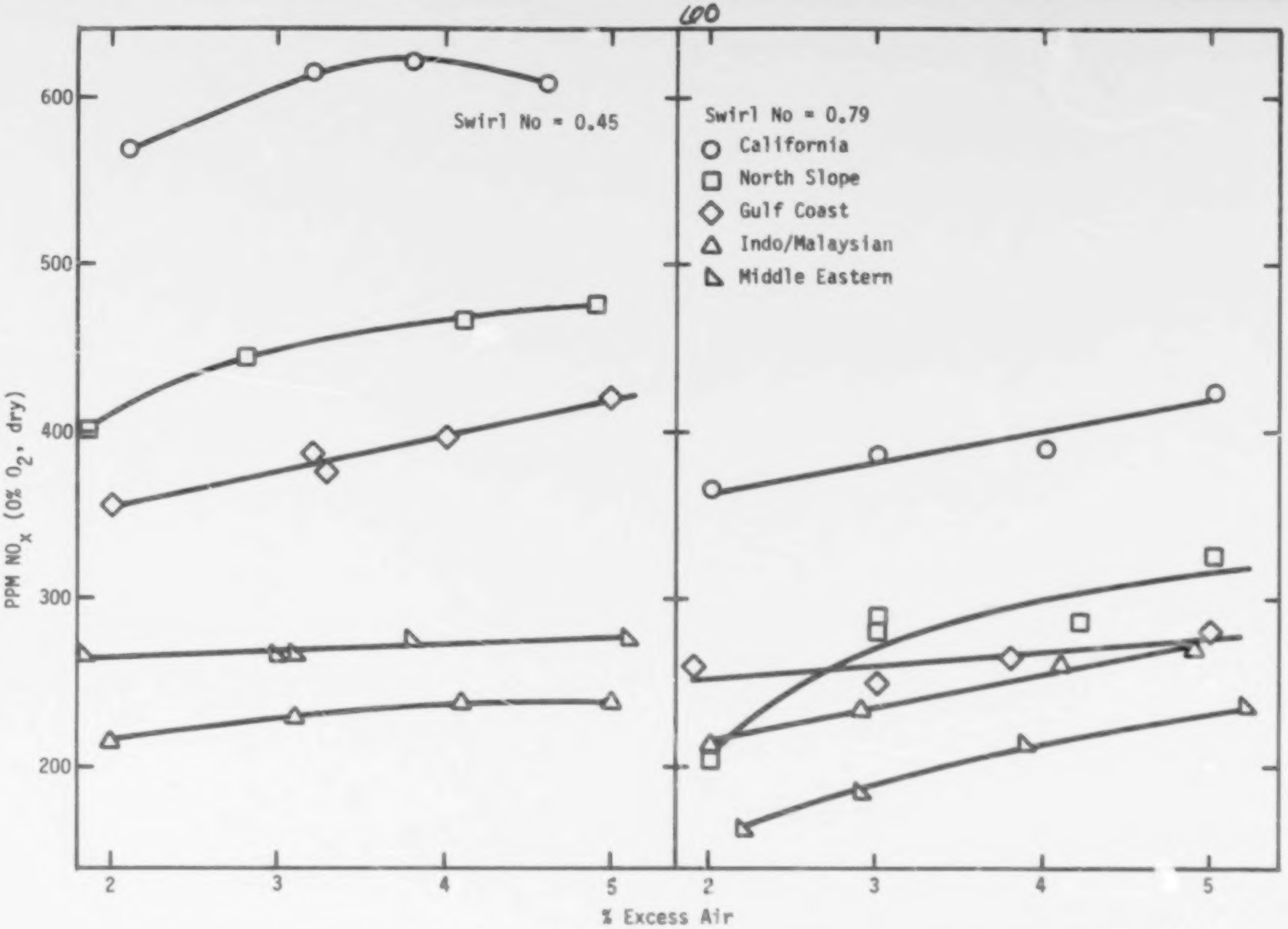


Figure 5. Influence of Fuel Type on NO_x Emission for a Single Atomizer in Two Swirl Levels.

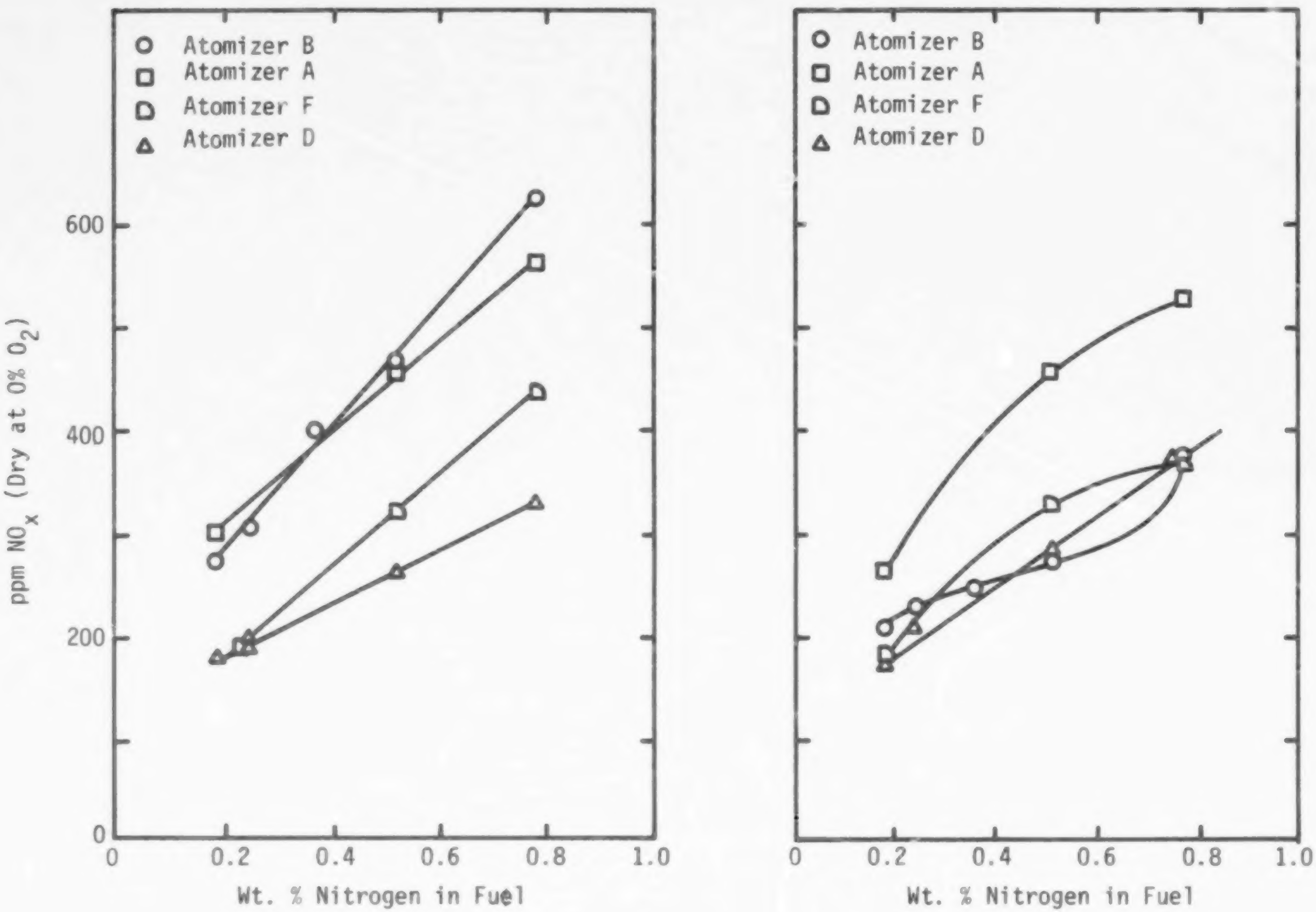


Figure 6. Influence of Atomizer Type at Two Swirl Levels.

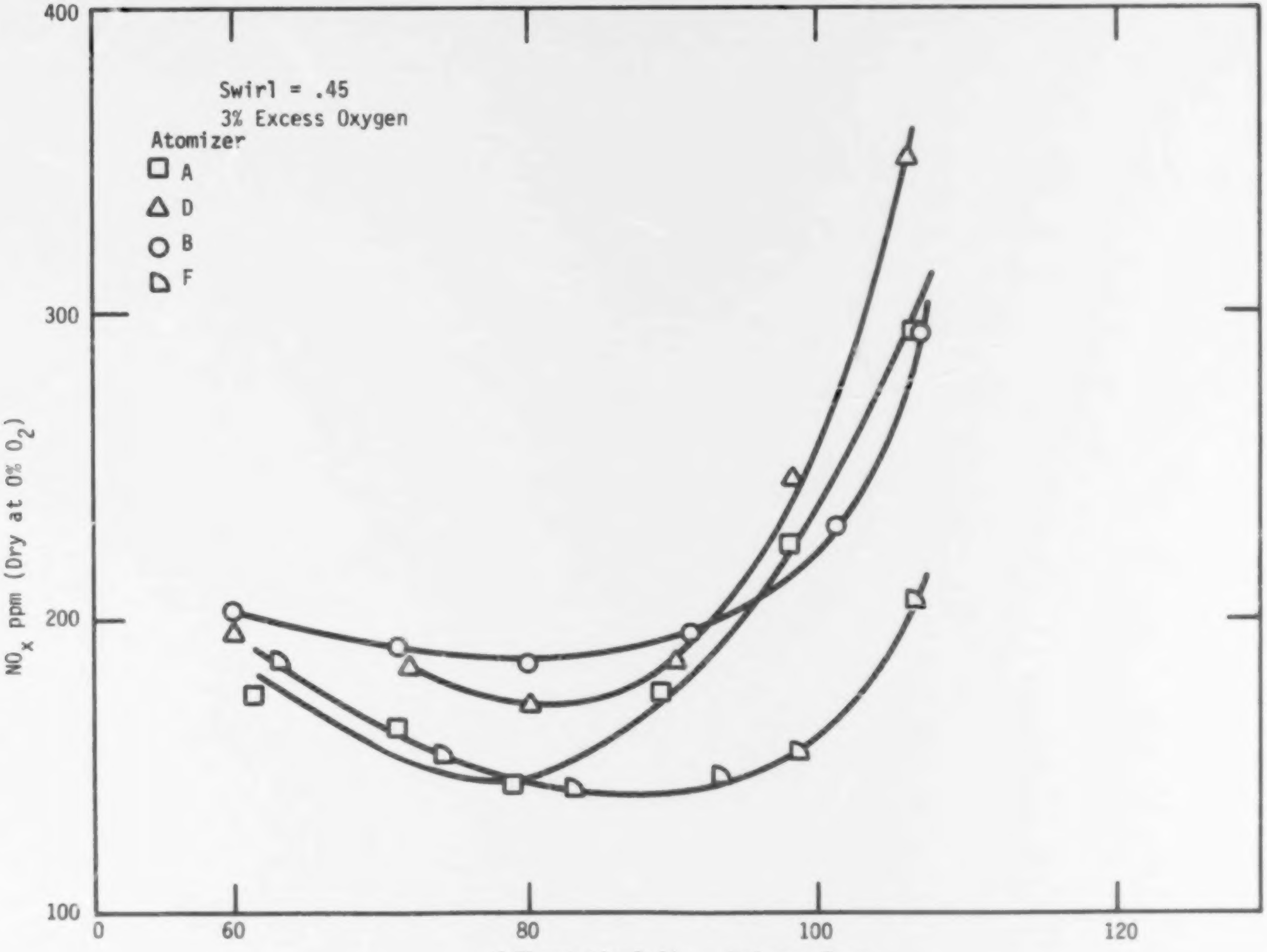


Figure 7. Comparison of NO_x Emission From Four Atomizers Under Staged Combustion.

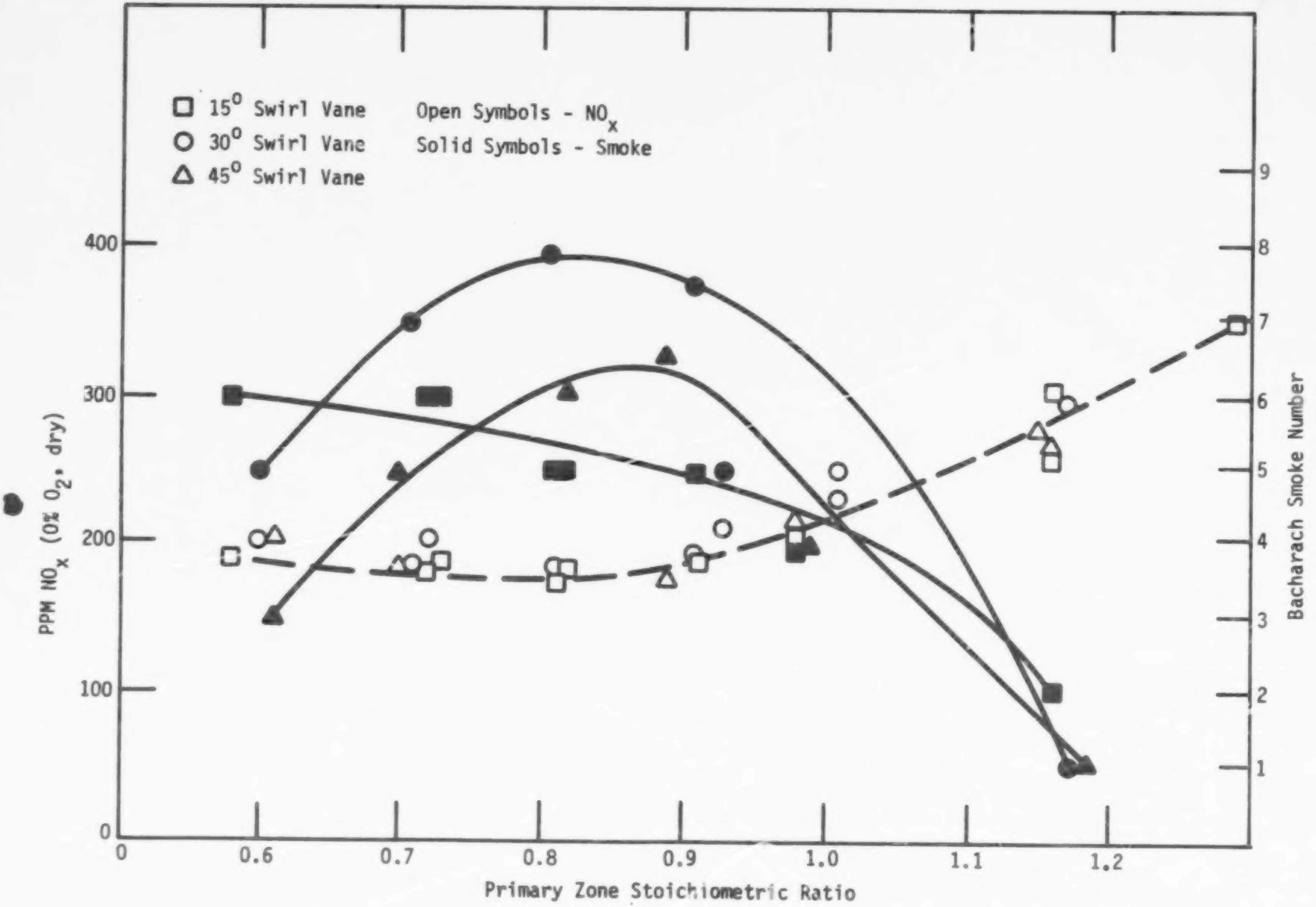


Figure 8. Influence of Swirl Level on NO$_x$ and Smoke Emissions Under Staged Combustion.

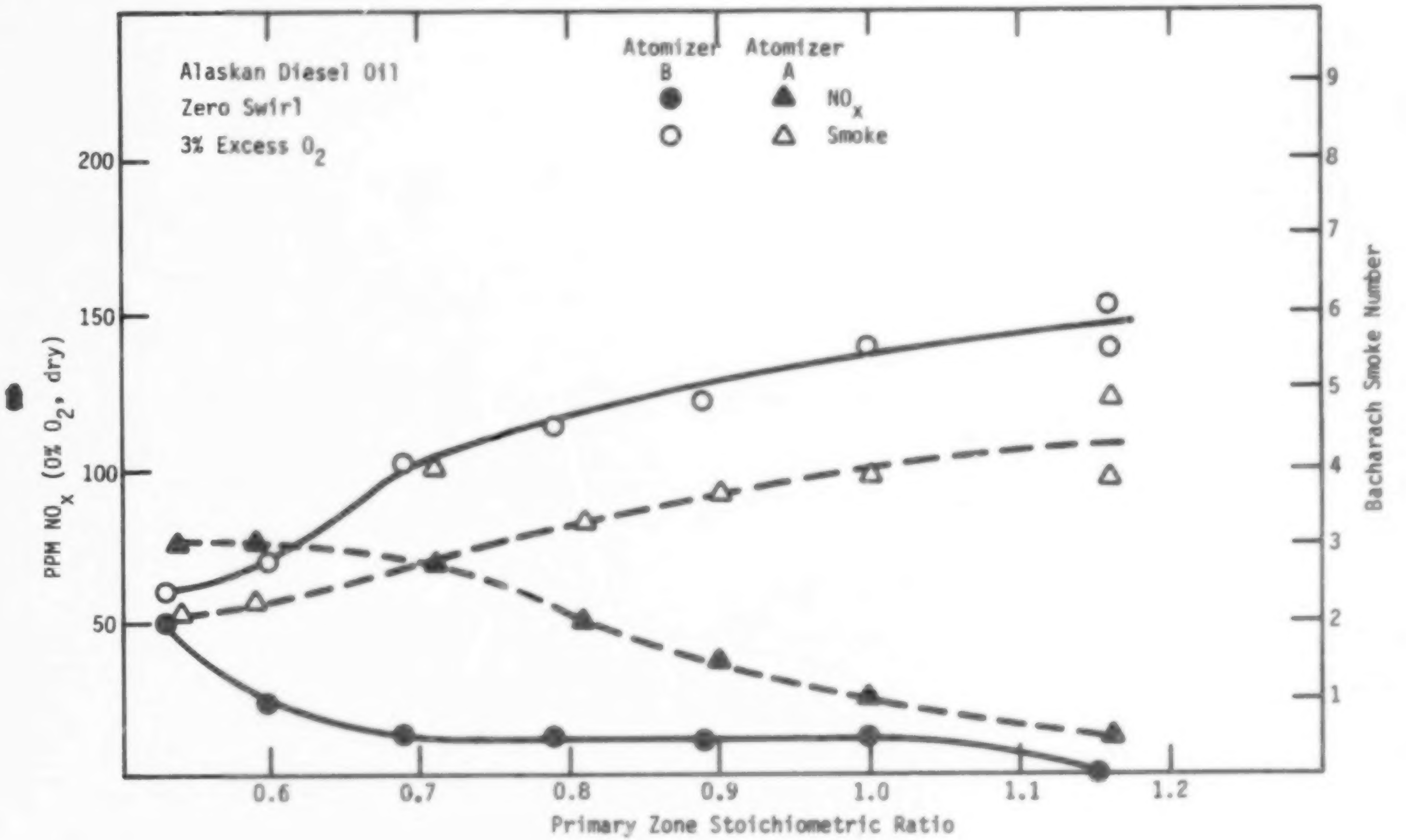


Figure 9. Influence of Atomizer Type on NO_x and Smoke Emissions Under Staged Combustion - North Slope Diesel Oil.

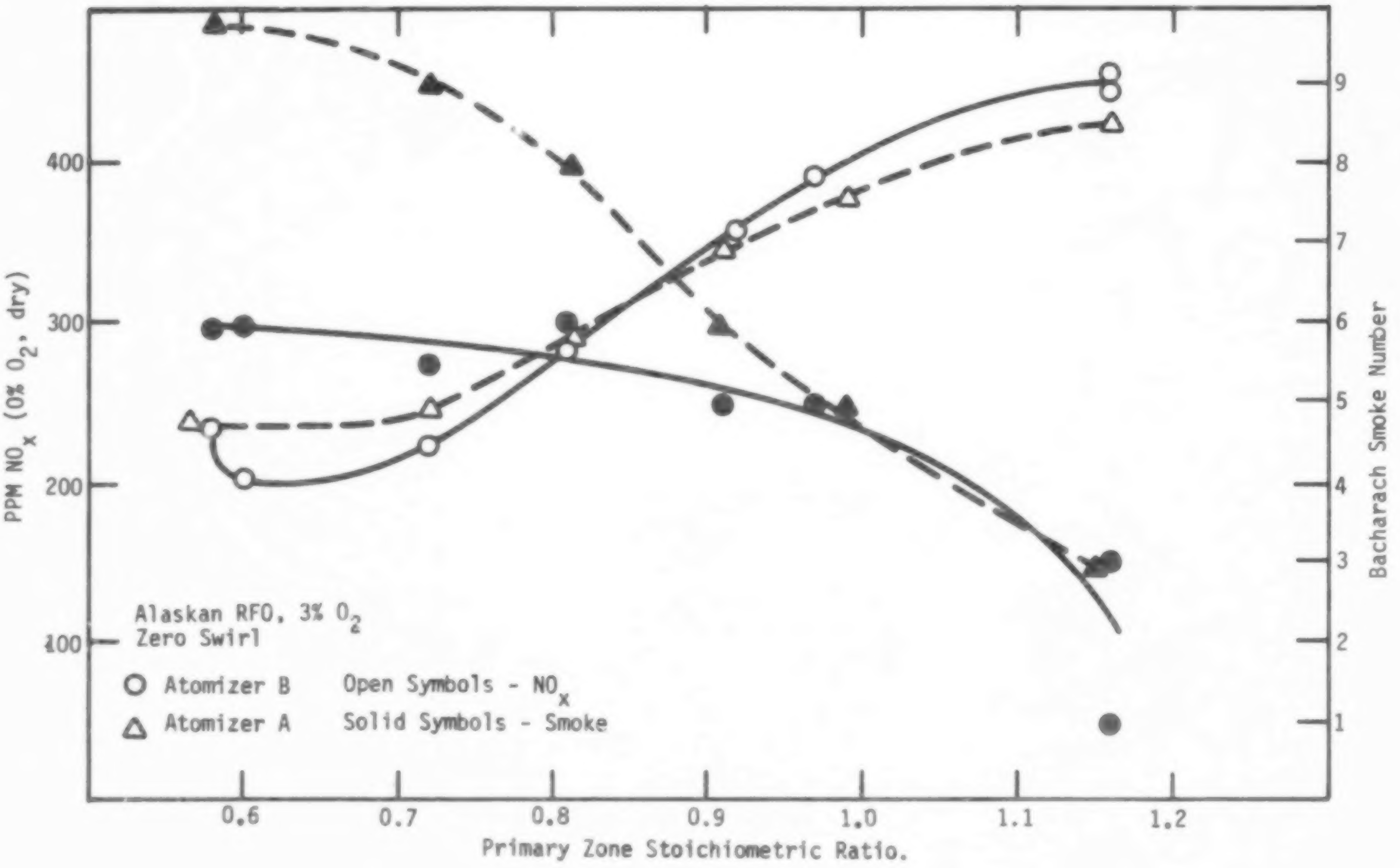
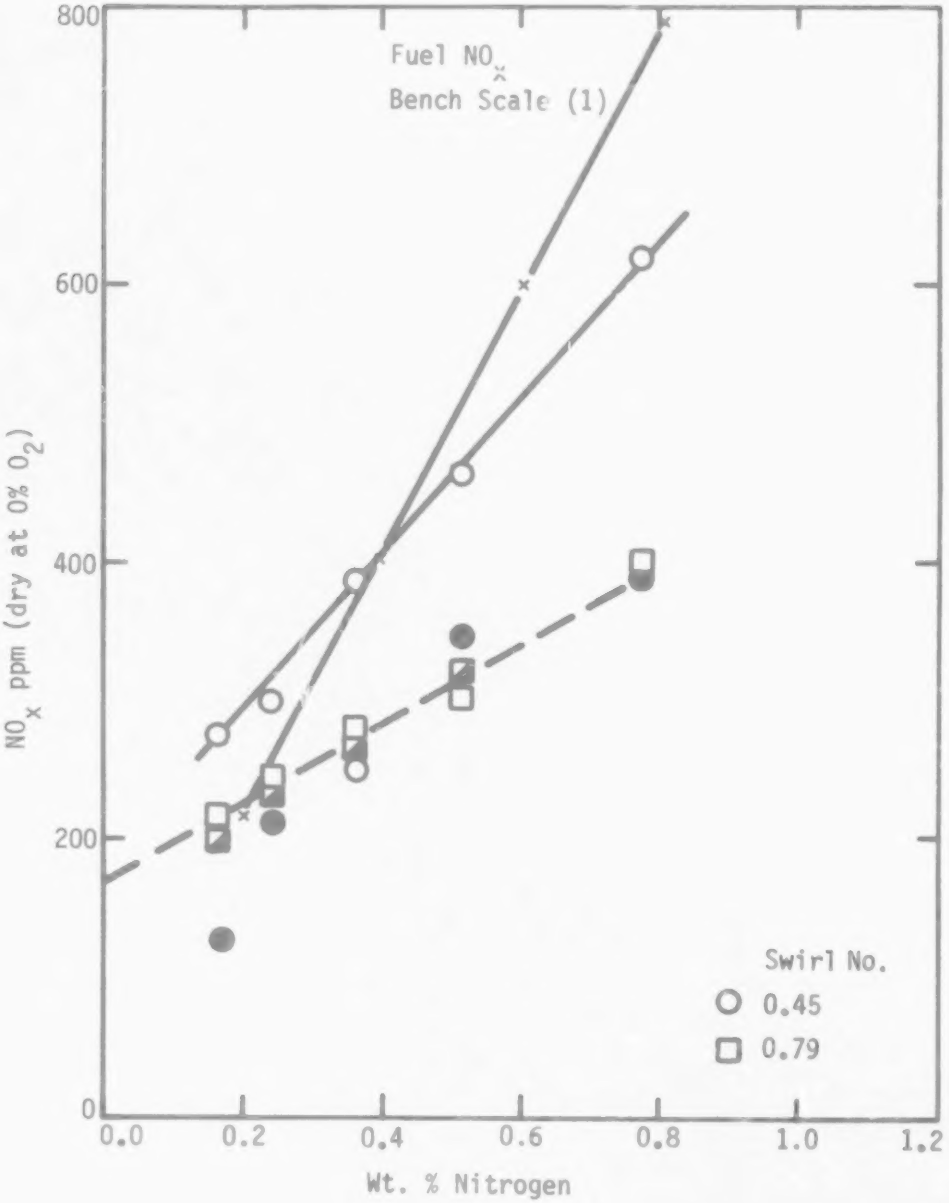


Figure 10. Influence of Atomizer Type on NO_x and Smoke Emissions Under Staged Combustion - North Slope Bunker C.



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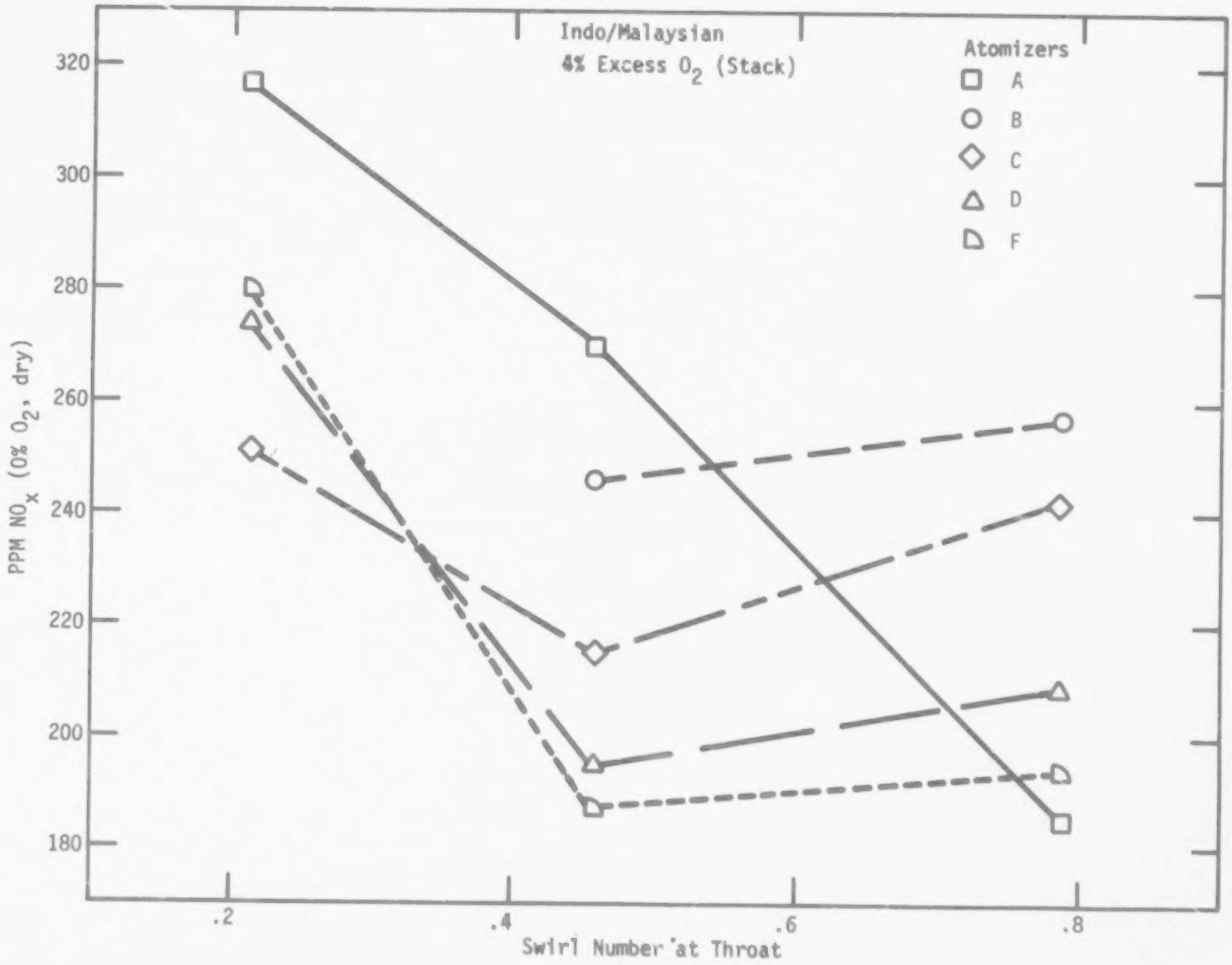

Figure 12. NO_x Emissions as a Function of Swirl Number for Five Atomizers.

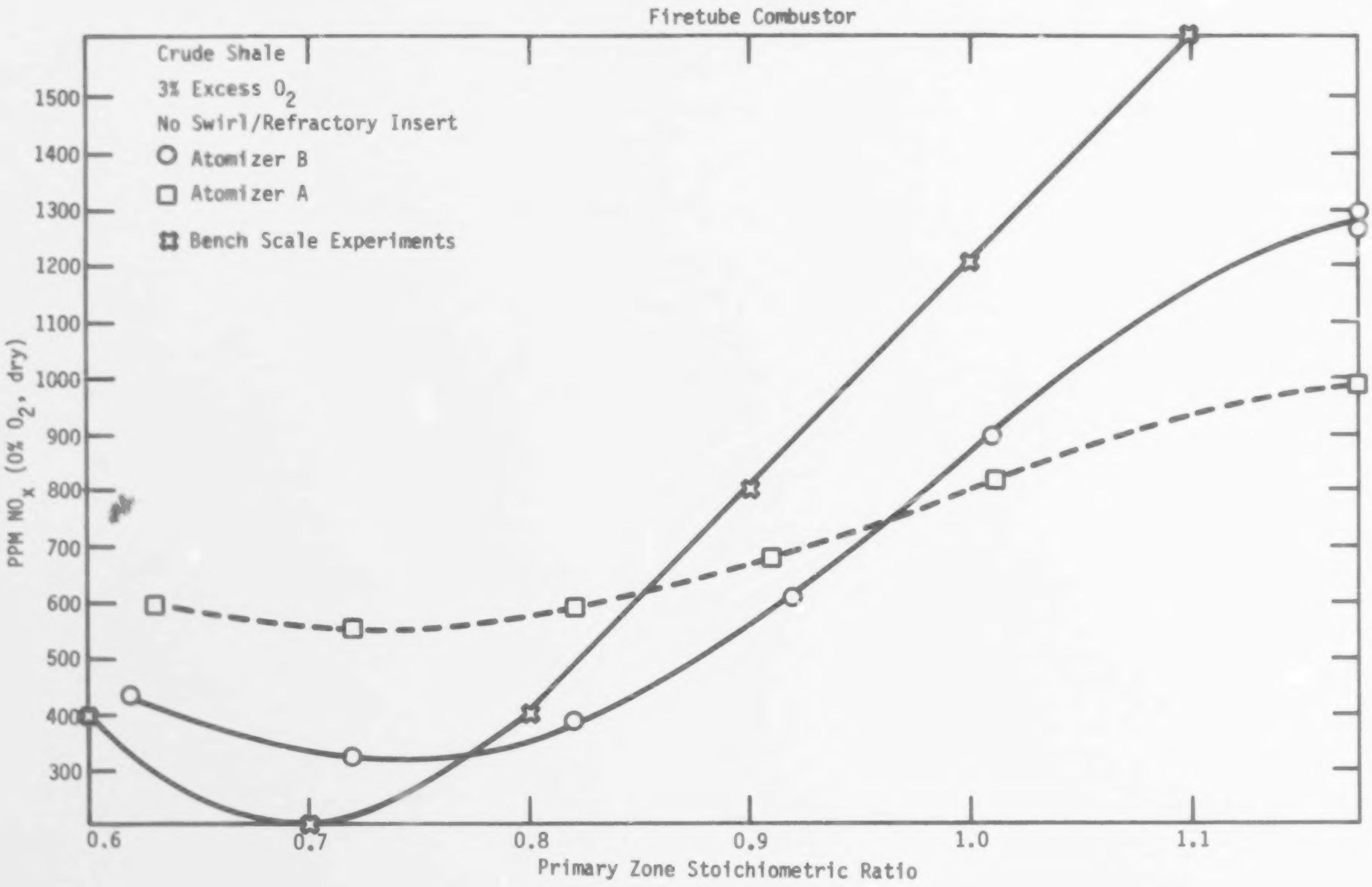

Figure 13. NO_x Reduction - Comparison of Bench Scale Experiments With Cold Wall Combustor.

TABLE I. LIST OF COMMERCIAL ATOMIZERS

ATOMIZER	DESCRIPTION
A	Internal mixing, air/steam assist, swirl chamber and pintle
B	Ultrasonic air assist
C	Internal mix, prefilming, air/steam assist, pintle
D	Y-jet internal mixing, air/steam assist
E	Y-jet internal mixing, air/steam assist
F	Y-jet internal mixing, air/steam assist
G	Y-jet internal mixing, air/steam assist swirl cap
H	Low pressure Y-jet internal mixing, swirl cap air assist

TABLE II. SELECTED FUEL OIL PROPERTIES

	1	2	3	4	5	6	7	8
Property	N. Slope Diesel	Middle Eastern	Indo/ Malaysian	Diesel Fuel Marine	Gulf Coast	N. Slope Bunker C	California	Shale Oil
Ultimate Analysis								
Nitrogen %	0.007	0.18	0.24	0.24	0.36	0.51	0.77	2.08
Sulfur %	0.31	0.67	0.22	0.51	2.44	1.63	1.63	0.63
Asphaltene %	-	3.24	0.74	0.036	7.02	5.6	5.18	1.33
API Gravity @ 60°F	33.1	19.8	21.8	33.1	13.2	15.6	15.4	20.3
Gross Heat of Combustion Btu/lb	19,400	19,070	19,070	19,430	18,240	18,470	18,470	18,290
Vanadium ppm	-	25	101	<0.1	45	67	44	<0.3

TABLE III. RATIO OF NO_X EMISSIONS AT INTERMEDIATE AND HIGH SWIRL LEVELS FOR FOUR ATOMIZERS AND FOUR FUELS

	ATOMIZER			
FUEL	A	B	C	F
2	1.07	1.26	0.98	0.91
3	1.46	0.96	0.94	0.96
6	0.96	1.52	0.84	0.93
7	1.02	1.53	0.84	1.15

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THE GENERALIZATION OF LOW EMISSION COAL BURNER TECHNOLOGY

By

D. M. Zallen, R. Gershman, M. P. Heap and W. H. Nurick
Energy and Environmental Research Corporation
Santa Ana, California 92705

ABSTRACT

This paper describes the development of a low NO_x pulverized coal burner. Results are presented from a series of tests designed to define optimum burner design parameters at three scales 10, 50 and 100 Btu/hr heat input. NO_x emissions were found to be most sensitive to burner zone stoichiometry and fuel injection parameters. Results are presented for three bituminous coals. The use of dry sorbents for SO_2 control is discussed and results are presented which suggest that low NO_x coal burners may provide optimum conditions for combined NO_x - SO_x control using flame zone sorbents.

NOMENCLATURE

SR	Stoichiometric Ratio = (air/fuel) actual/ (air/fuel) stoichiometric
T	Temperature
SA	Swirl angle
S	Swirl number = $\frac{G_\phi}{G_x R} = \frac{\text{Angular momentum}}{\text{Axial momentum x characteristic radius}}$
ppm	Parts per million by volume on a dry basis and reduced to zero percent excess air
Primary Air	Air in fuel injector
Secondary Air	Burner air in coannular passage around the fuel injector
Tertiary Air	Air used for staging

SUBSCRIPTS

1	Air with coal in fuel injector
2	Air in the coannular flow passage around fuel injector
3	Staging air injected from separate ports located at some radial distance from the burner centerline

ACKNOWLEDGMENTS

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SECTION I

INTRODUCTION

An increase in the direct combustion of coal, either pulverized and burned in suspension or crushed and burned in fixed or fluidized beds, represents the only near term solution to decrease our dependence upon the import of foreign petroleum products because of increased utilization of coal. However, the increased use of coal enhances environmental problems associated with its extraction, transportation and utilization. Coal contains several trace compounds which have the potential to produce atmospheric pollutants during the combustion process. This paper is concerned with the generalization of technology which is controlling the emission of two pollutants, nitrogen oxides (NO_x) and oxides of sulfur (SO_x) from pulverized coal-fired combustors. Direct coal combustion represents the major source of nitrogen oxides emitted by stationary sources. Consequently, unless appropriate emission control technologies are applied an increase in the utilization of coal in direct fired combustors has the potential to significantly increase NO_x emissions.

Historically, application of NO_x control to utility boilers represents the most cost-effective approach to controlling total emissions from stationary sources. Emissions from coal-fired utility boilers have been estimated to account for 32 percent of all emissions from stationary sources. The EPA has established an intensive program to demonstrate control technology for pulverized coal-fired boilers; industrial as well as utility, which will prevent adverse impact on the environment in the event of increased coal firing in water wall boilers. Technical goals have been established for 1985 which are equivalent to 20 percent of the existing New Source Performance Standards (NSPS) for NO_x emissions. These goals are to be met by combustion modification techniques (i.e., changing the process by which fuel and oxidant are brought together then how reaction occurs and heat is released). These techniques have been successful in allowing boilers to comply with NSPS.

However, the 1985 technical goal might well represent the limit of their application since the near term requirement dictates that the control techniques be compatible with existing state-of-the-art boilers. Major modifications to the boiler would involve an extensive development program and necessarily the control technology would take time to be accepted by the utility industry.

Two processes are involved in the emission of nitrogen oxide from coal-fired boilers: 1) the oxidation of molecular nitrogen (thermal NO), and 2) the oxidation of nitrogen contained in the coal (fuel NO). Insofar as bulk gas temperatures are low, and thermal NO formation is mainly restricted to the heat release zone, combustion modifications which minimize peak flame temperatures and maximize combustion product quench rates will control its production. Fuel NO formation is determined by the conditions in the heat release zone; fuel residence time under oxygen-deficient conditions being the major factor in minimizing fuel NO production. Peak flame temperatures, product quench rates and residence time in fuel-rich zones can be controlled by burner design parameters (e.g., method of fuel and air injection, distribution of axial and tangential velocity, burner geometry, etc.). Effectiveness of these parameters as a means of controlling NO_x emissions from pulverized coal flames has been demonstrated in both pilot- and large-scale systems. These investigations have led to the development of a burner which can be applied to existing boiler designs to satisfy the technical NO_x emission goals described above. This burner is based upon the concept of distributed mixing* which minimizes NO_x formation while satisfying other process requirements (e.g., heat flux distribution, burnout, etc.).

The basic burner design features, the watertube simulators, and the ancillary equipment used in this study have been described in detail elsewhere (1). The results of earlier pilot-scale studies were used to develop a prototypte burner whose performance has been demonstrated at a scale and under conditions which are similar to actual watertube boilers. This paper summarizes the results obtained to date with single burners at three scales with different coals, and discusses the implications associated with multiple burner firing. In addition to NO_x control, the DMB has been used in a series of investigations to assess the possibility of in-situ sulfur capture using dry sorbents. The sorbents were added to the coal prior to pulverization and it appears that the DMB has the potential to satisfy the process requirements for both NO_x and SO_x control.

---

* Distributed Mixing Burner (DMB)

SECTION 2

LOW NO_x BURNER DEVELOPMENT

Pulverized coal combustion in burner stabilized, turbulent diffusion flames is a complex phenomenon which cannot be described fully by a mathematical model. Consequently, the development of the low NO_x DMB based upon the original pilot-scale concept has progressed emperically. Two different burner systems have been tested to date. These are:

- A burner with a divided secondary throat which allows control of axial and tangential velocity in two annular air streams. Fuel is injected axially from an annulus surrounding a central oil gun used for ignition.
- A simple double concentric burner with fixed swirl vanes in both the annular fuel and secondary air channels. Swirl is used in the fuel injector to enhance flame stability. This burner design was selected because of ease of construction in providing for exact geometric and velocity similarity at three scales.

The velocity characteristics of the two burners are illustrated in Figure 1 for 50 x 10^6 Btu/hr burners operating at 4 percent overall excess air as a function of the burner zone stoichiometric ratio. The influence of several burner and operational parameters have been investigated with both burners, and the composition of the three different coals which have been used to date are given in Table 1.

The burner with the divided throat allows a wide variation in the distribution of both axial and tangential velocity of the secondary air stream and provides for considerable control over flame shape with the wide angle burner exit (35^o half angle). Three basic flow patterns were observed in both cold and hot flow (see Figure 2). These were:

- Type A with all axial flow except for an annular toroidal recirculation zone which provided for flame stability.

- Type B with an axial toroidal recirculation zone.
- Type C in which the flow attached to the combustion chamber wall producing a wall jet.

The transition from A through C occurred as the swirl level in the outer channel increased. Figure 2 also presents sketches of two general flame types which were obtained with a narrower burner exit (25^{o} half angle). The shorter flame is much more compatible with existing boiler designs.

The low sufur Utah coal listed in Table 1 was used for the major portion of the tests performed using the divided throat burner. The general effects of overall excess air and burner zone stoichiometry were as expected. NO_x decreased as the overall excess air and the burner zone stoichiometry was decreased. Unlike more conventional burner designs, emissions were relatively insensitive to variations in load for a given burner size. Various burner exit geometries were tested and it was found that flame stability was improved with a narrower burner exit whose length was equal to the throat diameter. A schematic of the divided secondary throat burner is presented in Figure 3. Figure 4 compares NO_x emissions for the divided secondary throat burner at two scales. The burner was designed for constant air velocity and geometric similarity. The larger burner yielded lower NO_x values. For the scaling principle used, the size of the fuel-rich burner zone would be proportional to a linear burner dimension implying that the residence time in this region is also proportional to burner scale for a given velocity. This provides one simple explanation for the lower values obtained at larger scale. However, other parameters may well be important.

Further development studies have been carried out with the less complex double concentric burner shown in Figure 5 at three design firing rates of 12.5, 50 and 100 x 10^6 Btu/hr. The use of a single channel for the burner throat provided for a more straightforward interpretation of the results, and also allowed "exactly similar" burners to be produced at three scales. All three burner scales employed similar distribution of tangential velocity and similar locations for the outboard staged air injectors, and had a burner exit half angle of 25^{o}. The NO_x emission characteristics of this low NO_x DMB design have been evaluated and the influence of the following operational and design parameters assessed:

- Burner zone stoichiometry. Both the overall burner zone stoichiometry and the stoichiometry of the primary airflow.
- Burner parameters including the degree of swirl in both the fuel and secondary air channels. The location and velocity of the outboard staged air injectors and the location of the fuel injector.
- Firing rate.
- Fuel type.

Typical results obtained to date are presented below.

BURNER ZONE STOICHIOMETRY

The effect of burner zone stoichiometry for a range of excess air levels is shown in Figure 6 for three different scales at comparable conditions. The two large burners were tested in the large watertube simulator. Burner zone stoichiometry is calculated based upon the total fuel flow and the air being delivered with the primary and secondary streams (total air minus outboard staged air). Comparison of the large and intermediate scale burner test results (see Figure 6) show a moderate increase in NO_x with scale. However the results obtained with the smallest burner were highest of all. It is possible that variations in combustor configuration may contribute to this difference since the smallest burner was fired in a different combustor than the two large burners but at a similar burner zone heat release rate.

For a given fuel injector geometry variations in the amount of primary air will not only change the local stoichiometry in the zone close to the fuel injector it will also affect the primary velocity and the results presented in Figure 7 may be attributed to changes in either or both of these properties. The data indicates that the primary stoichiometry for optimum burner performance is dependent upon burner scale. This is probably associated with the fact that the residence time in the fuel rich zone is different for the three burner scales.

BURNER PARAMETERS

The operation of the simple burner shown in Figure 5 involves a reduction of secondary airflow as the burner zone stoichiometry is reduced. This reduces the tangential momentum of the secondary stream; thus, any balance between primary and secondary momenta will be affected as the burner zone stoichiometry is reduced at a given primary flow. It was found necessary to provide the burner with fixed annular swirl vanes in the primary pipe to ensure flame stability under staged conditions. This simple vane system not only provides some tangential momentum, but also acts to divide the coal stream into separate jets. Figure 8 compares NO_x emissions for various primary swirl vane angles and it appears that a vane angle of 45° provides the optimum performance. NO_x emissions were also found to be sensitive to the level of swirl in the secondary stream. In general, NO_x emissions were reduced as the swirl level increased, as can be seen in Figure 9.

The effect of both the location and velocity of the staged air jets was investigated. Typical results are presented in Figure 10. Optimum performance appears to be obtained with low velocity, and staged air injection with the injectors located two burner-throat-diameters from the burner axis. For the smallest burner tested the emissions and flame stability were found to be sensitive to the location of the fuel injector. However, good performance was obtained with the two larger burners when the fuel injector was located at the throat of the burner.

FUEL TYPE

It can be seen from the results presented in Figure 11 that the performance of the low NO_x DMB is dependent upon fuel type for the 12×10^6 Btu/hr burner. There are considerable differences in the emission characteristics for the same burner with different fuels, which is not necessarily associated with overall nitrogen content since under highly staged conditions emissions from the three coals are comparable. The results obtained at 100×10^6 Btu/hr compared to that shown for 12×10^6 Btu/hr for the West Virginia and Utah coals suggest that the effect of fuel type is also associated with scale. For example at the smaller scale the Utah coal gives a lower value of NO_x than the West Virginia coal. This characteristic is reversed at the larger scale.

SECTION 3

SULFUR CAPTURE

Control of oxides of sulfur can be achieved by one of three general methods: 1) the sulfur can be removed prior to combustion, either in a gasifier or by physical or chemical cleaning; 2) sulfur may be absorbed by a solid during the combustion process itself as in a fluidized bed combustor; and 3) the sulfur oxides can be removed from the products of combustion. It is known that certain compounds have the potential to produce sulfates, and certain coals with high calcium and sodium ashes give high sulfate ash contents. The use of sorbents such as limestone to remove sulfur oxides has been applied unsuccessfully in several instances (2,3). Both small-scale studies and field test have suggested that the retention efficiency of such sorbents can be quite low and under these conditions the mass of sorbent required to achieve the necessary level of SO_2 control is excessive. However, sorbent utilization efficiency has been shown to be sensitive to such parameters as temperature, stoichiometry, particle size, etc. A preliminary series of experiments have been carried out with the low NO_x DMB with the intention of assessing whether or not low NO_x operation enhances the possibility for in-situ sulfur capture, since the DMB provides a temperature/time stoichiometry history that should maximize the sorbent utilization.

Preliminary tests were carried out using the Utah coal in a small refractory tunnel furnace to assess the effect of sorbent dispersion, flame temperature, the method of fuel/air contacting, and combustion air staging upon sulfur capture. The effectiveness of the sorbent was assessed by measuring the SO_2 content of the combustion products. The two most significant results of these small-scale studies were that the sulfur capture was enhanced considerably when the sorbent was mixed with the coal prior to pulverization, and that increasing flame temperature enhanced rather than inhibited the effectiveness of the sorbent. The influence of sorbent dispersion can be readily understood since to achieve high sorbent efficiencies it is necessary that the sorbent be uniformly mixed throughout the combustion gases. The effect of increasing temperature was somewhat surprising since with limestone as the additive, it could be concluded that maximum flame temperatures would produce dead-burning, and therefore, limit the activity of the sorbent.

A series of preliminary exploratory investigations were also carried out in the small watertube simulator with a 12 x 10^6 Btu/hr low NO_x DMB. The objective of these preliminary studies was to assess the effect of sorbent type, (calcium and sulfur compounds were used), sorbent ratio and coal type upon sulfur capture, as well as to determine (1) whether there were significant advantages of operating under low NO_x conditions, and (2) whether or not sulfur capture influenced NO_x emissions. It is important to note that the DMB design is such that under non-staging conditions the coal/air mixing profile still provides for a slow mixing control core. Consequently even though unstaged the DMB flame characteristics will be quite different from those produced with typical commercial turbulent burners. The results presented in Figures 12 and 13 for a low and high sulfur coal, respectively, are typical of the results obtained in these preliminary experiments. Since exhaust SO_2 concentration was used as the criterion for sulfur capture, care was taken in the sampling procedure to prevent condensation in the sample lines. Also, measurements were made of SO_2 concentrations before and after tests with additive to ensure that the sulfur dioxide levels were reproducible. With a calcium-to-sulfur molar ratio of one, 50 percent of the sulfur was captured by the additive for both the high and low sulfur coals, and with this particular calcium-to-sulfur ratio there appeared to be a significant effect of operation under staged combustion conditions. In these preliminary investigations no attempt was made to optimize the burner configuration for both NO_x reduction and sulfur capture.

The results presented in Figure 14 show that there appears to be no effect of sulfur capture upon NO_x emissions. From gas phase kinetic considerations it might be expected that SO_x/NO_x would influence the overall NO_x emissions when the burner was operated staged. The results obtained to date do not indicate that this is a significant factor.

SECTION 4

DISCUSSION

The primary design objectives of the low NO_x DMB are:

- To maximize both the rate and total volatile evolution from the coal particle. This does not only refer to nitrogen specie, but also to fuel fragments since gas phase stoichiometry will be dependent upon the volatile fuel fraction.
- To provide an initial oxygen-deficient zone which minimizes NO production, but then to add sufficient oxygen to the rich combustion products to maximize the rate of decay of nitrogenous specie (such as NH_3, NO, HCN) to molecular nitrogen.
- To provide optimum residence time and sufficient temperature to maximize N_2 production.
- To maximize char residence time in the fuel-rich zone since some nitrogen will remain in the solid with the potenital for forming NO during burnout.
- To provide second stage air ensuring complete burnout.
- To produce an overall oxidizing envelope around the fuel-rich core thereby minimizing the possibility for corrosion on the combustor walls.

These objectives are obtained by providing for the optimum interaction betwen the primary fuel jet and the swirl-stabilized recirculation zone, together with delayed air addition from the outboard staged air injectors.

Figure 15 compares the NO_x levels achieved at three different scales for a low NO_x DMB. Figure 16 presents the NO characteristics for the optimum configuration at the same three scales. The differences between the various scales may be associated with the variation in fuel residence time for different scales, or burner/chamber interaction affecting bulk gas temperatures, and therefore, reaction zone temperatures.

In addition to the optimization of burner design parameters and the development of empirical scale criteria, the program to generalize low emission coal burner technology has three other important objectives which are:

1. Construct a fuel data base which will establish whether it is necessary to vary the burner design as a function of coal properties.
2. Determine the effects of burner/chamber interaction and develop information for multiple burner configurations.
3. Provide direct comparison between prototype low NO_x burners and commercially available burners.
4. To assess the effect of low NO_x operation on the emission of other pollutants such as fine particulate matter and sulfur oxides.

A comparison between the prototype and commercial burners will provide information enabling the performance of the low NO_x DMB to be assessed when operating under more practical conditions.

Three investigations are planned to assess the affect of burner/chamber interactions on the performance of the low NO_x DMB. These include:

- Single-wall arrays to assess the effect of burner/burner spacing, burner/sidewall spacing and the use of shared staged air injectors.
- Opposed-wall firing.
- Off-axis firing. The minimum NO_x emissions achievable by the DMB concept may provide excessive flame lengths. In order to overcome flame impingement upon combustion chamber walls, four burners will be tested firing off-axis in order that the interaction between the various long flames will prevent wall impingement.

The preliminary results involving the use of dry sorbents for SO_2 capture are encouraging, and currently investigations are underway to provide confirmatory results by closing the sulfur balance after capturing the solid. Figure 17 summarizes the results obtained to date with three additives, two coals and various additive/sulfur ratios. It can be speculated that the effectiveness of the DMB as a means of enhancing sulfur capture is associated with the following:

- Sorbent dispersion. Effective sorbent utilization requires that its concentration must be high and that it is evenly distributed in these regions where the sulfur specie are evolved from the coal. In the tests described above the sorbent was mixed with the coal before the pulverizer and therefore was evenly dispersed in the form of small particles.
- Sorbent activity. The sorbent is in contact with high sulfur concentrations initially after calcination at the time it is most reactive. Also the low NO_x DMB probably provides the optimum time-temperature history for maximum sorbent activity and minimal deadburning.
- Peak flame temperatures occur under fuel rich conditions. The sulfur and sorbent initially make contact under oxygen deficient conditions and probably form a sulfide which is more stable at higher temperatures than the sulfate. Consequently decomposition of the "sulfur containing sorbent" will be minimized.
- Reduced peak temperatures and low bulk gas temperatures. Low NO_x operation requires that peak temperatures are minimized thus ensuring maximum residual sorbent activity to capture sulfur in the bulk gases after the heat release zone. The fact that the sorbent is evenly dispersed will also tend to maximize sulfur capture in this region.

These preliminary results suggest that the use of a flame zone sorbent plus baghouse might well be a viable SO_x control technology for low sulfur Western coals or in addition to physical or chemical cleaning for high sulfur coals.

SECTION 5

SUMMARY

The increased utilization of coal for power generation has the potential for adverse environmental impact due to increased emissions of atmospheric pollutants. One of the pollutants, NO_x can be controlled by modifying the combustion process to maximize residence time under fuel rich conditions in order to prevent the formation of NO from nitrogen contained in the coal. The combustion of pulverized coal involves injection of the fuel and air through a burner whose function is to ensure ignition stability and complete combustion in the necessary volume. A burner has been developed which controls the rate of pulverized coal air mixing that not only satisfies normal process requirements but also minimizes the formation of nitrogen oxide. This concept was originally evaluated at pilot scale but it has now been demonstrated at a scale and in an environment which is typical of waterwall boilers. The low NO_x DMB has been tested at three scales using three bituminous coals and the results obtained to date can be summarized by:

- Under optimum design conditions NO_x emissions are typically below 200 ppm (dry at 0% O_2) for three burner scales (12, 50 and 100 x 10^6 Btu/hr).
- NO_x emissions are not independent of scale when a simple geometric scaling law is applied.
- The emission characteristics of the low NO_x DMB appears to be mildly dependent upon coal characteristics.

A preliminary series of investigations have been carried out to assess the use of the DMB to control both NO_x and SO_x by adding dry sorbents to the coal before the pulverizer. It was felt that the DMB would provide ideal conditions to maximize sorbent efficiency. Limestone mixed with the coal in calcium to sulfur molar ratios of 1, 2 and 3 gave 53, 73 and 88% reduction in SO_2 emissions respectively for a low sulfur coal. At low calcium/sulfur ratios SO_2 reduction is enhanced by low NO_x operation.

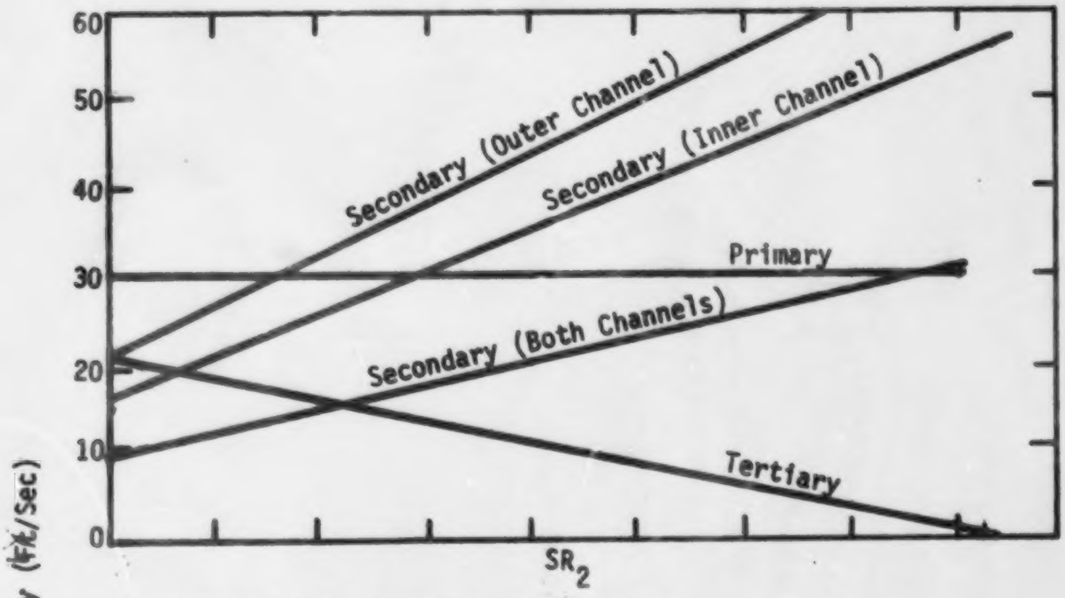
It should be noted that the impact associated with the use of this technology for SO_x control in field operating boilers requires a complete assessment. The most immediate areas requiring process and economic analyses are increased solids handling (both prior to and after combustion), mill capacity, fly ash characteristics (size distribution and resistivity), slagging and fouling in the boiler and the environmental problems associated with solids disposal. Should the development and small scale studies continue to provide encouraging results it is intended that the technology will be demonstrated in an industrial boiler fitted with an EPA low NO_x DMB.

REFERENCES

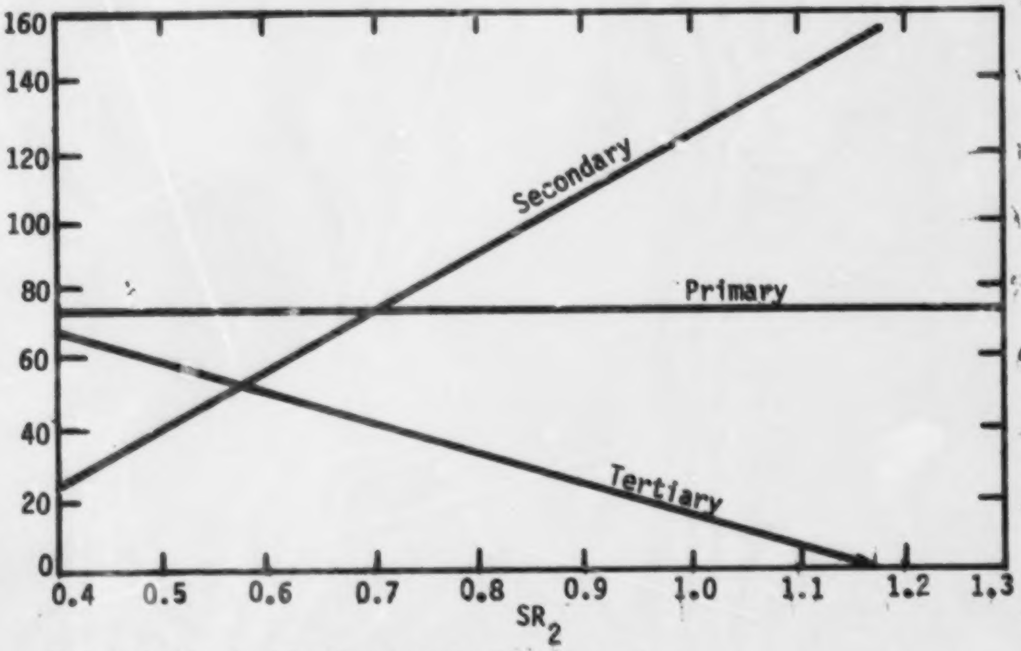
1. Gershman, R. E., M. P. Heap, and T. J. Tyson. Design and Scale Up of Low Emission Burners for Industrial and Utility Boilers. Proceedings of the Second Stationary Source Combustion Symposium, Volume 5, Addendum EPA 600/7-77-073e, July, 1977.

2. Attig, R. C. and P. Sedor. Additive Injection for Sulfur Dioxide Control - A Pilot Plant Study, National Air Pollution Control Administration, Report No. 5460, March, 1970.

3. Gartrell, F. E. Full Scale Desulfurization of Stack Gas by Dry Limestone Injection, Volume I, Tennessee Valley Authority, Chattanooga, EPA 650/2-73-019A, (PB-228 447), August, 1973.

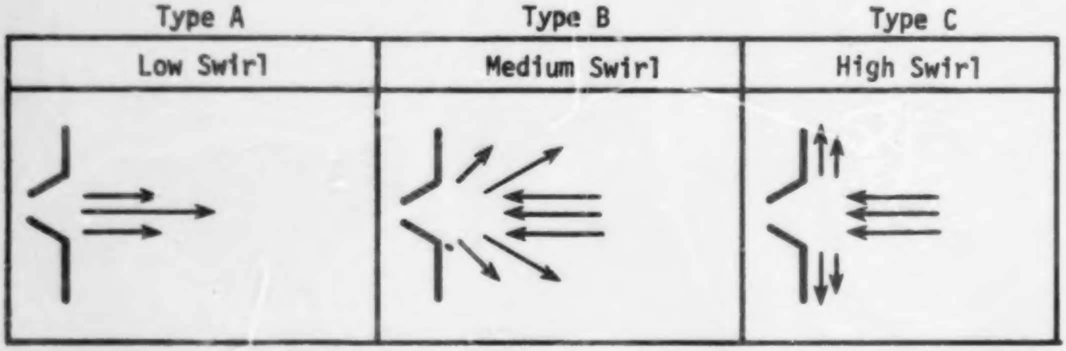


A.) Divided Secondary Throat Design.

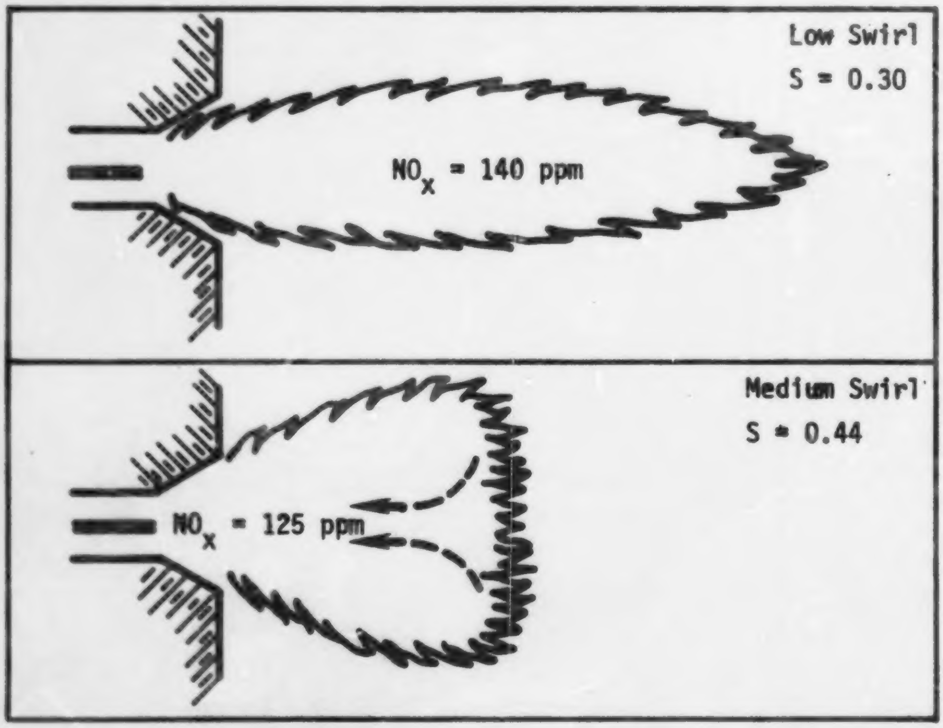


B.) Simple Double Concentric Burner Design

Figure 1. Air Velocity Characteristics for two 50 x 10^6 Btu/hr Coal Fired Distributed Mixing Burners.


Type A
Type B
Type C
Low Swirl
Medium Swirl
High Swirl

A.) Flame Types


Low Swirl
S = 0.30
NO_x = 140 ppm
Medium Swirl
S = 0.44
NO_x = 125 ppm

B.) Low NO_x Flame Shapes

Figure 2. Flame Characteristics for DMB.

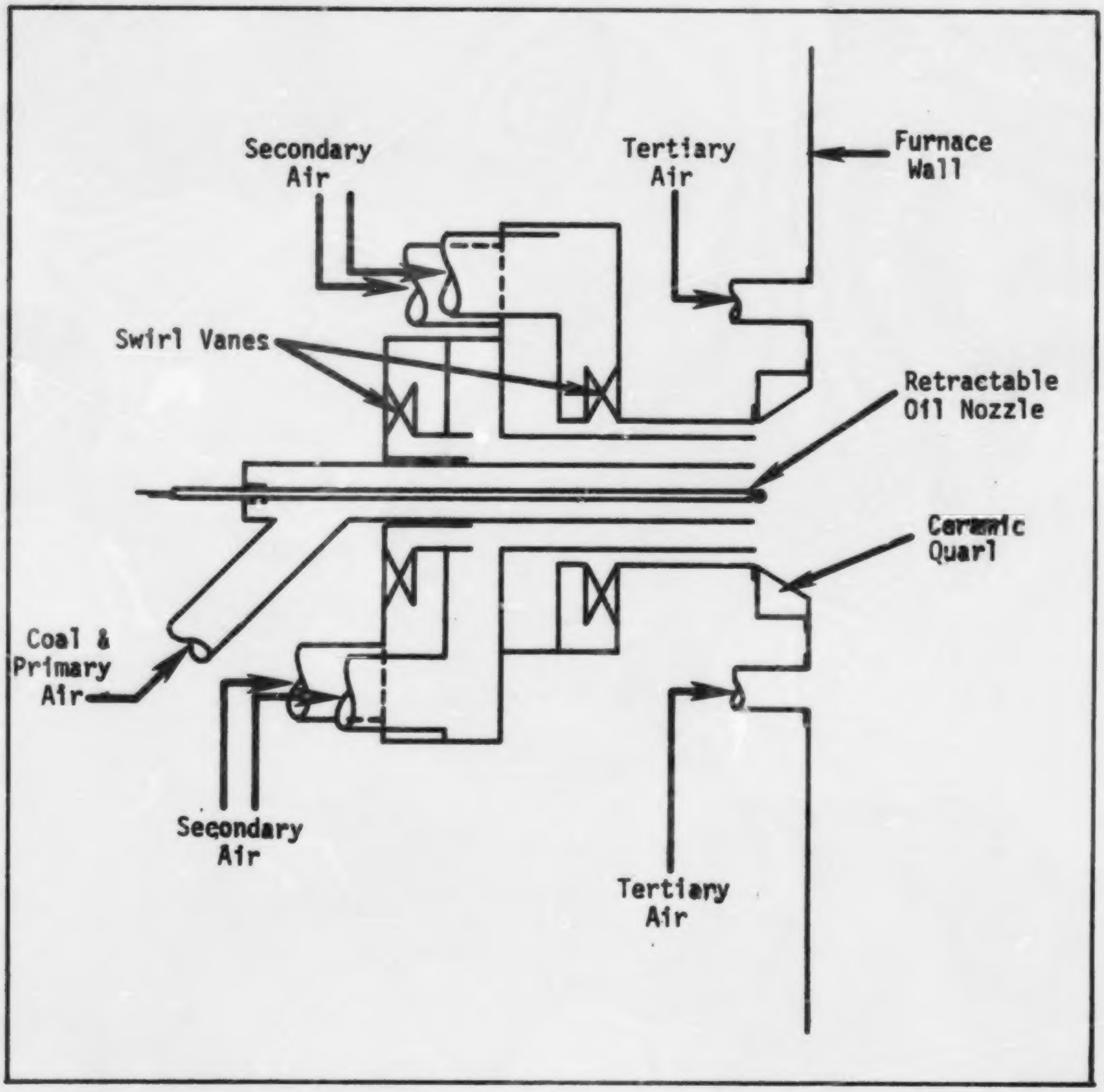

Secondary Air
Tertiary Air
Furnace Wall
Swirl Vanes
Retractable Oil Nozzle
Ceramic Quarl
Coal & Primary Air
Secondary Air
Tertiary Air

Figure 3. Divided Secondary Throat Burner Design.

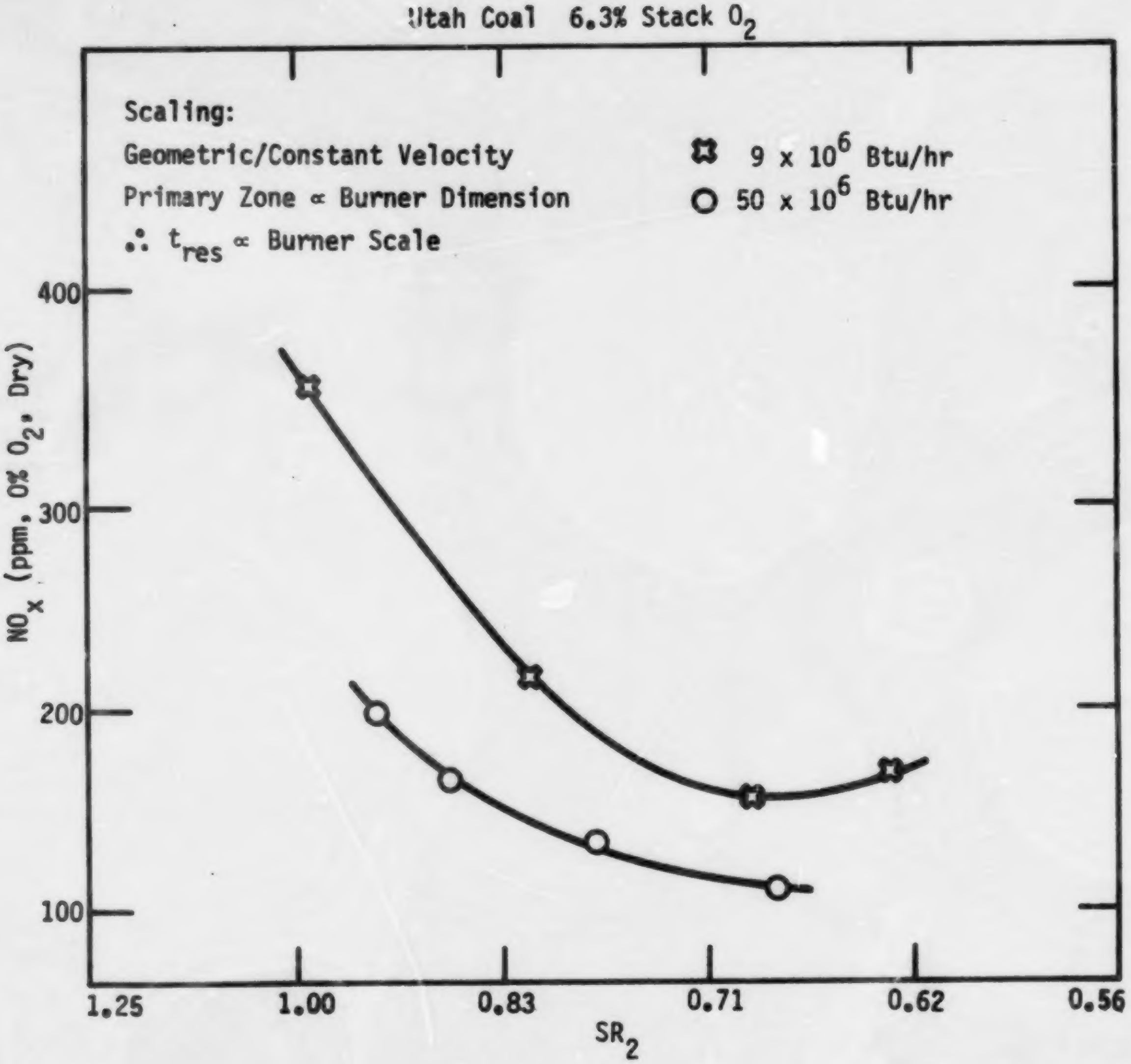


Figure 4. Comparison of NO_x Emissions at Two Burner Scales - Divided Secondary Throat Design.

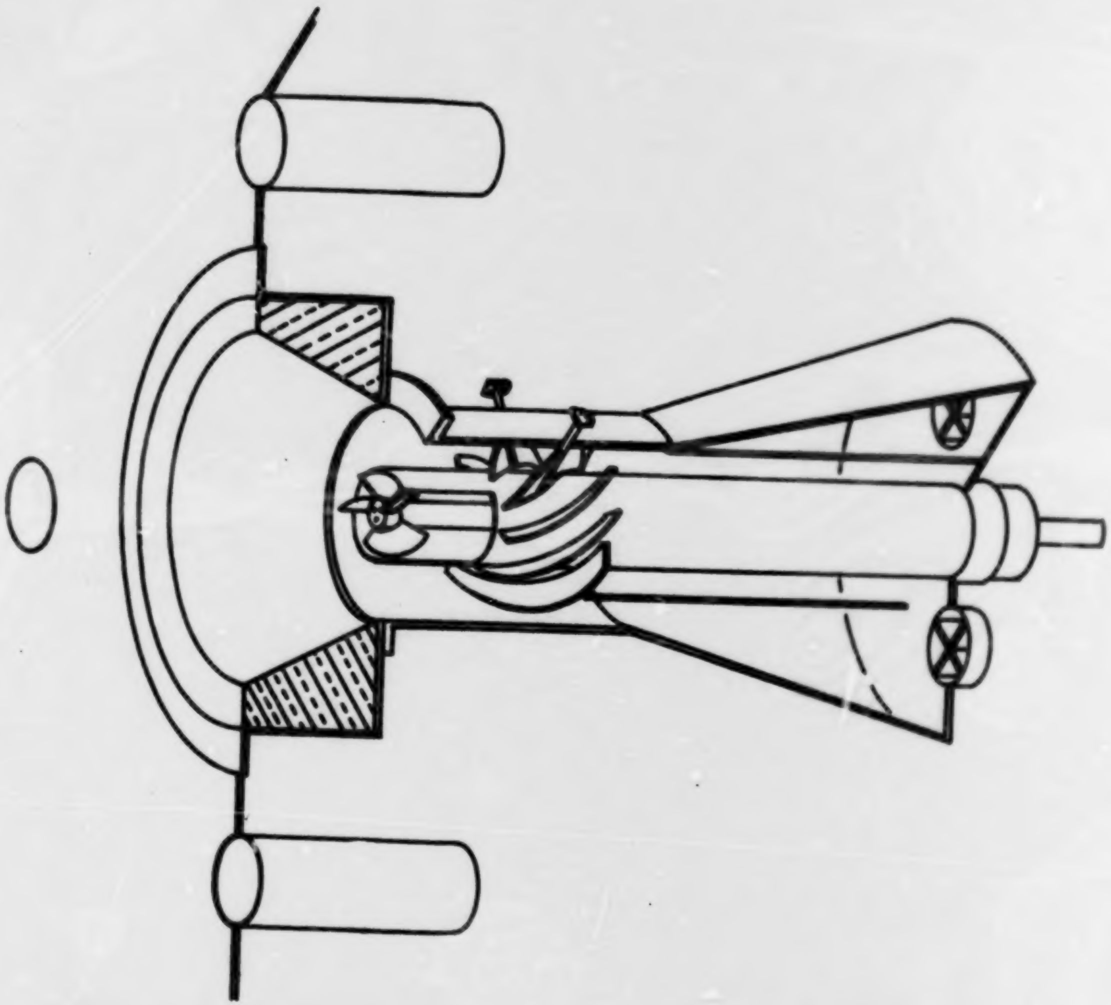


Figure 5. Low NO_x Development Burner - Simple Double Concentric Burner Design.

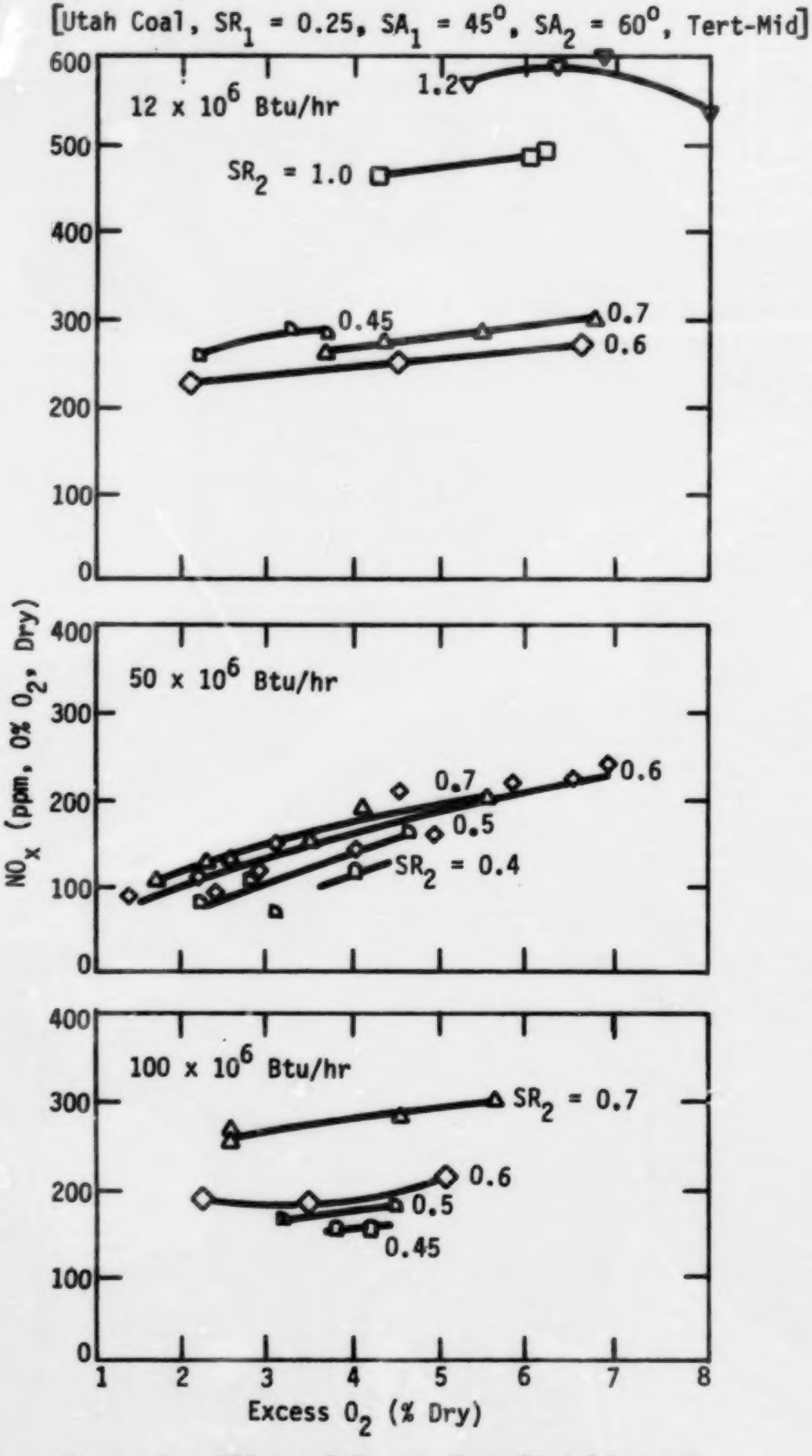


Figure 6. Effect of Burner Zone Stoichiometry.

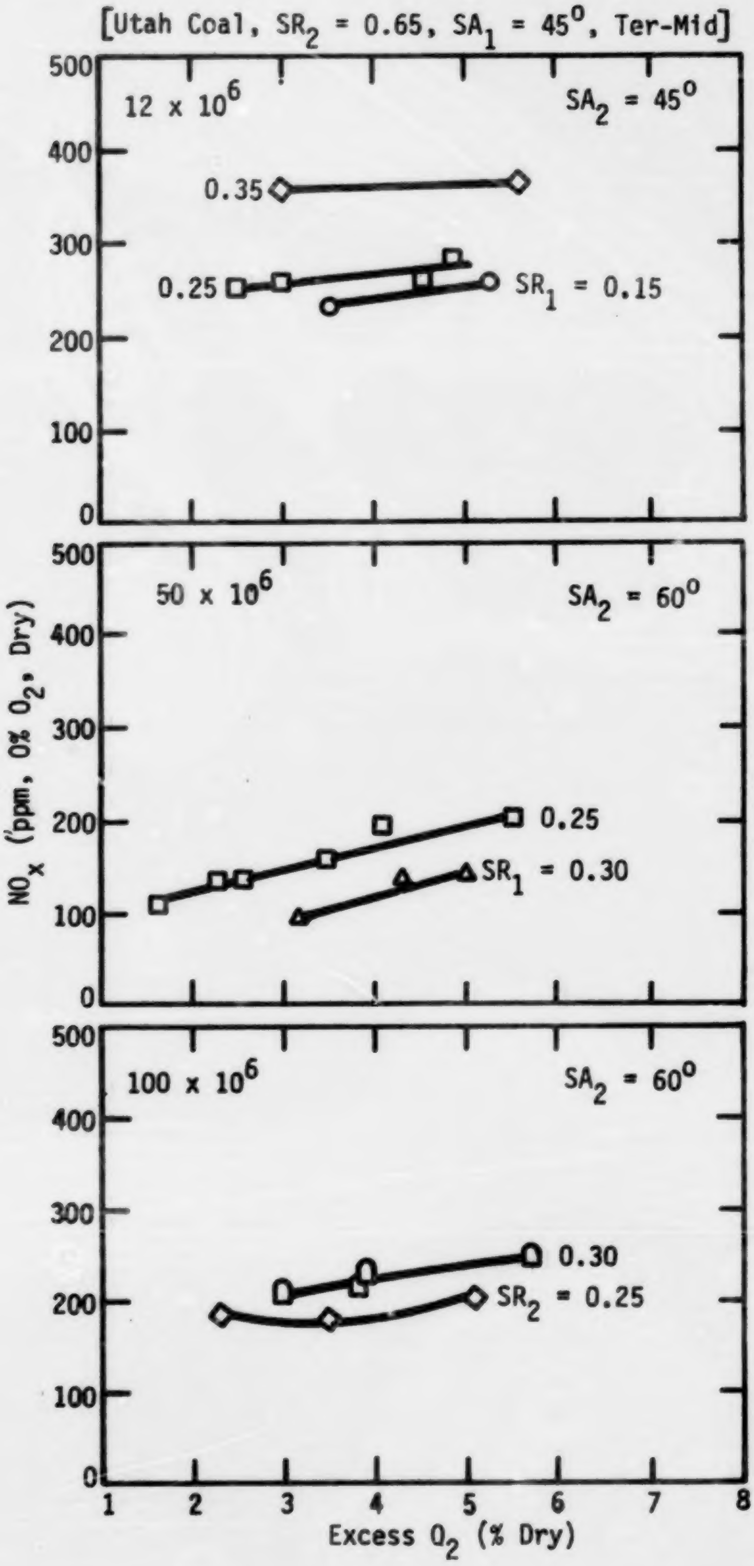


Figure 7. Effect of Primary Stoichiometry.

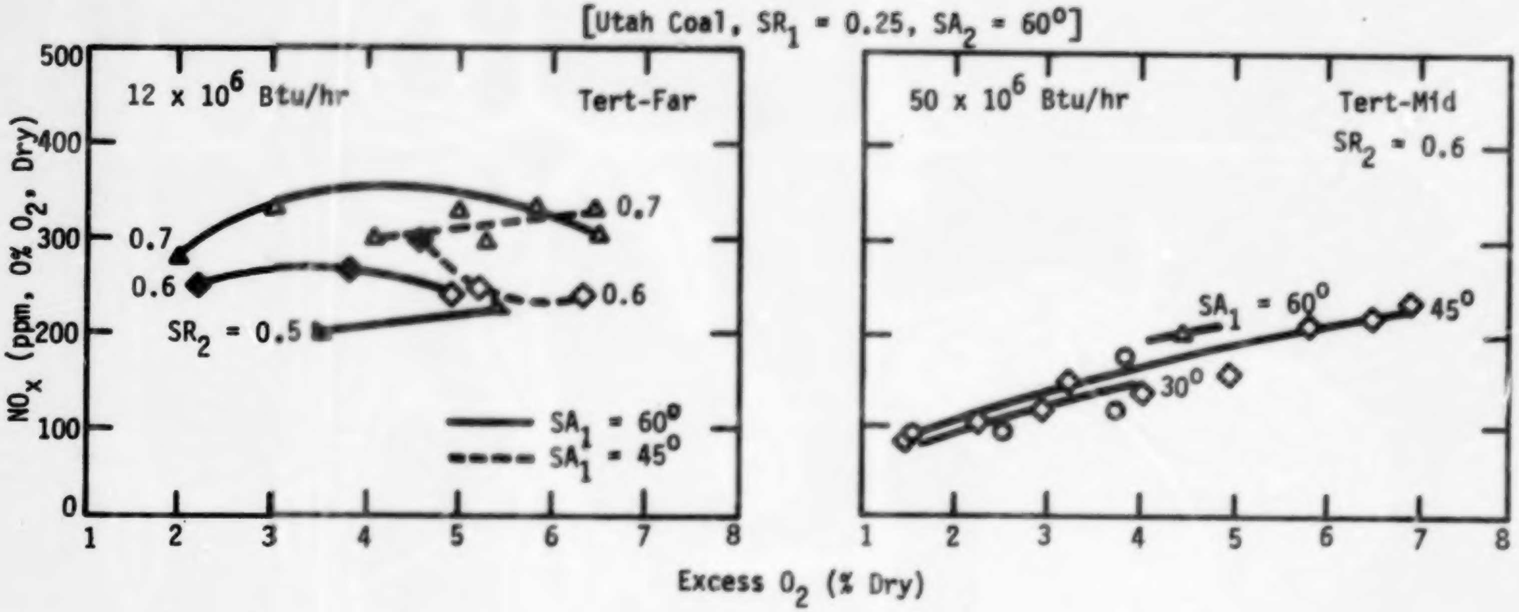


Figure 8. Effect of Primary Swirl.

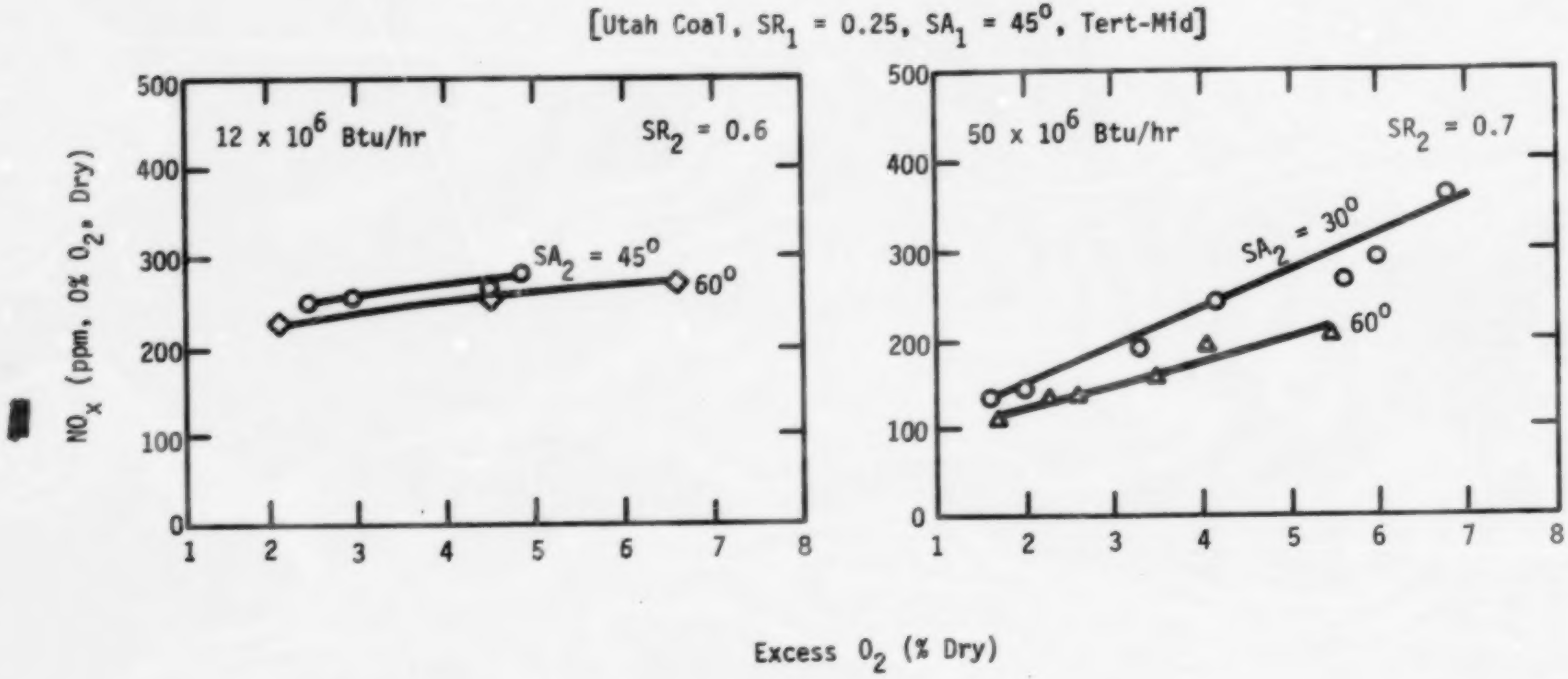


Figure 9. Effect of Secondary Swirl.

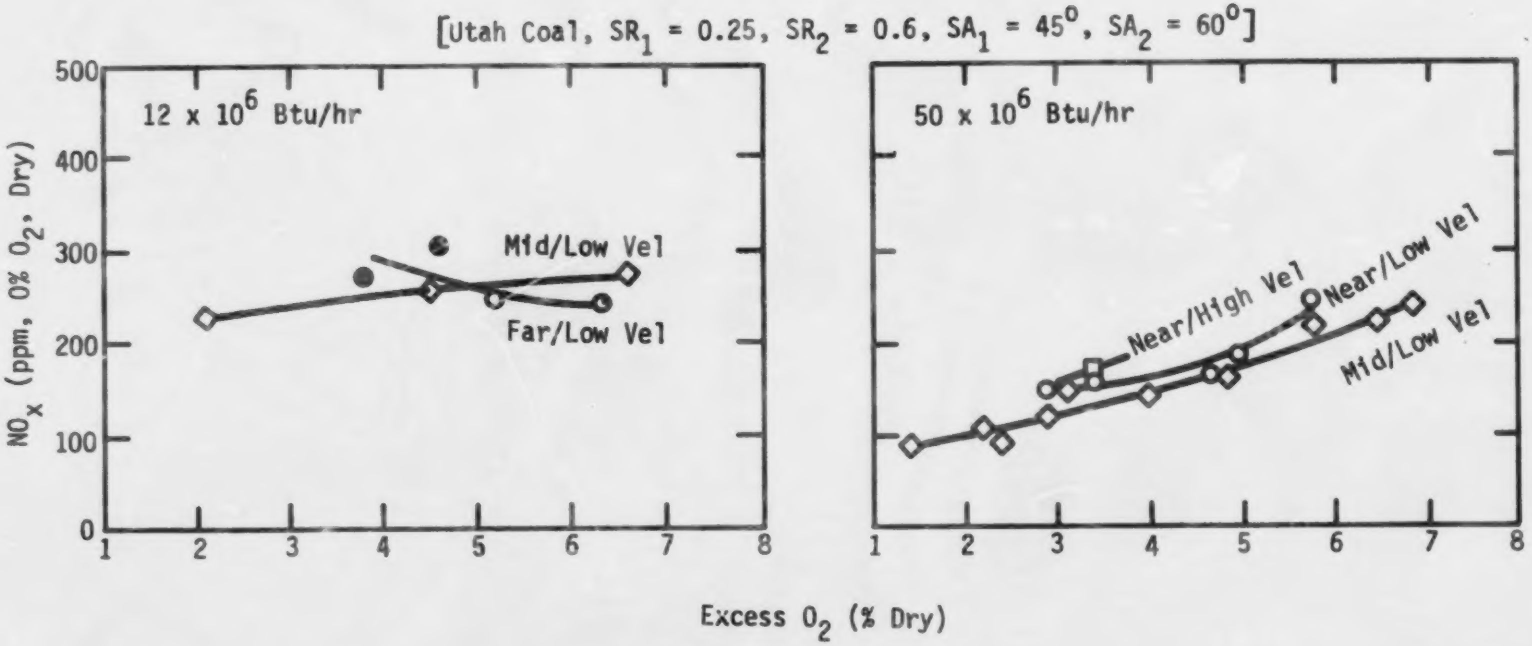


Figure 10. Effect of Tertiary Location and Velocity.

[SR_1 = 0.25, SA_1 = 45°, SA_2 = 60°, Tert-Mid]

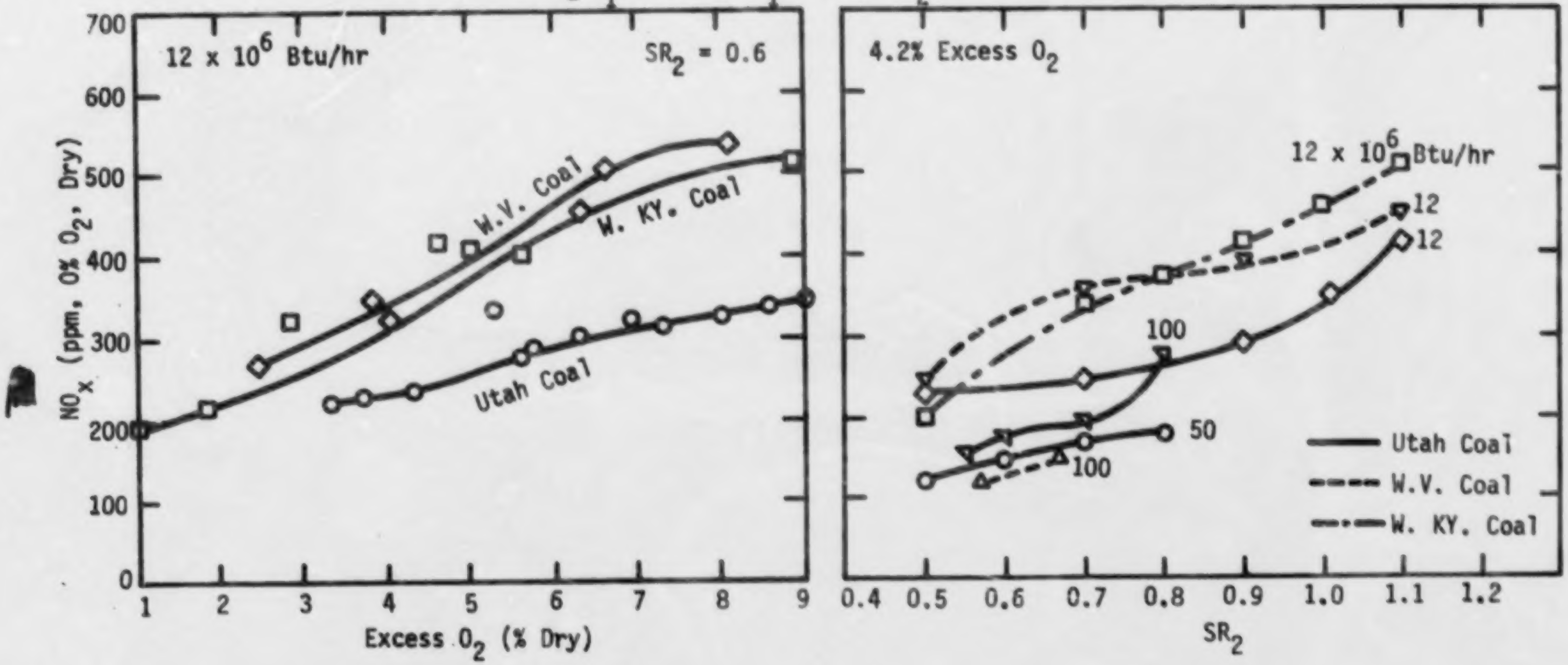


Figure 11. Fuels Performance.

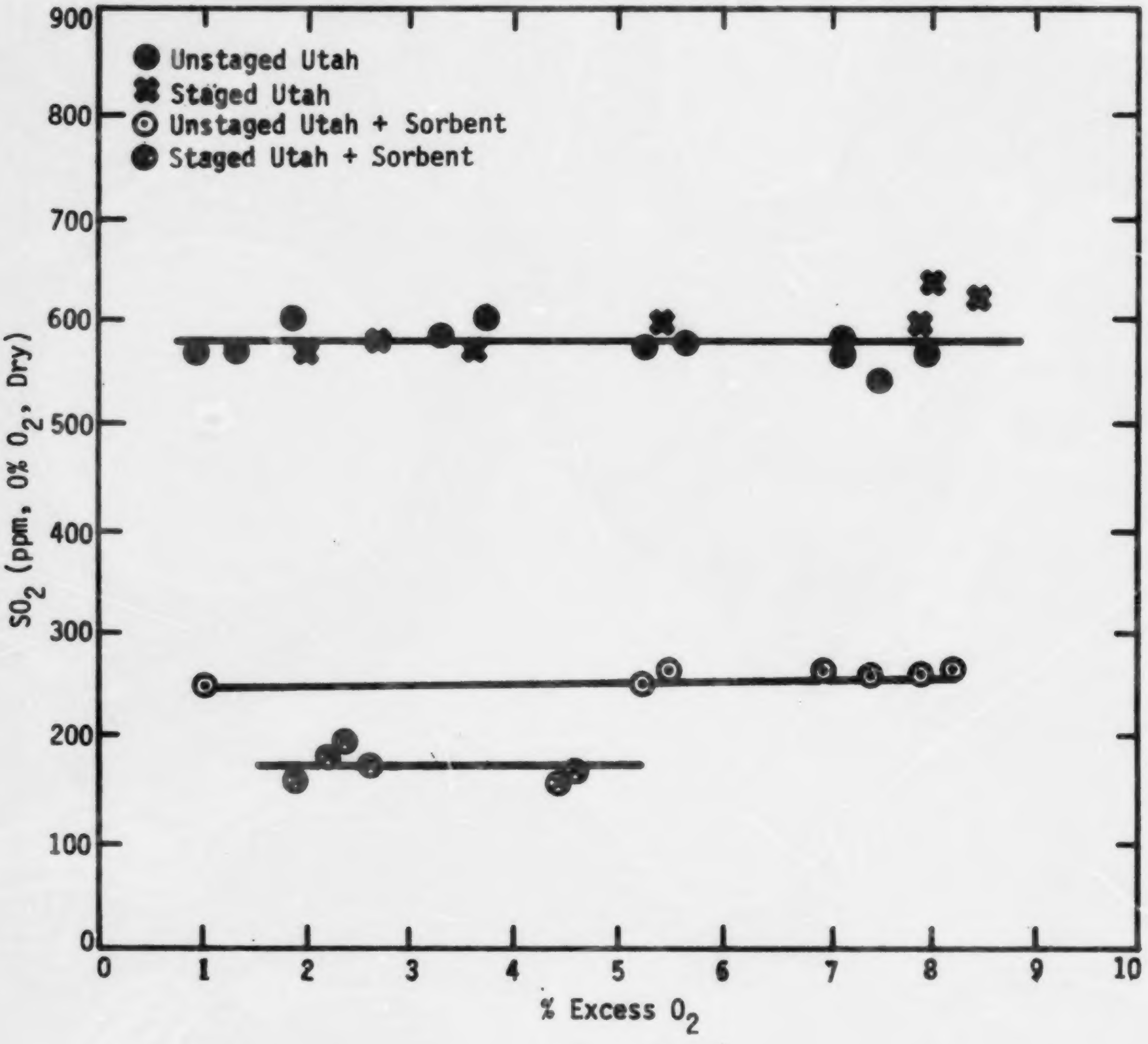


Figure 12. The Effect of the Addition of Limestone to the Utah Coal Prior to Pulverization on SO_2 Emissions (Ca/S = 1.0).

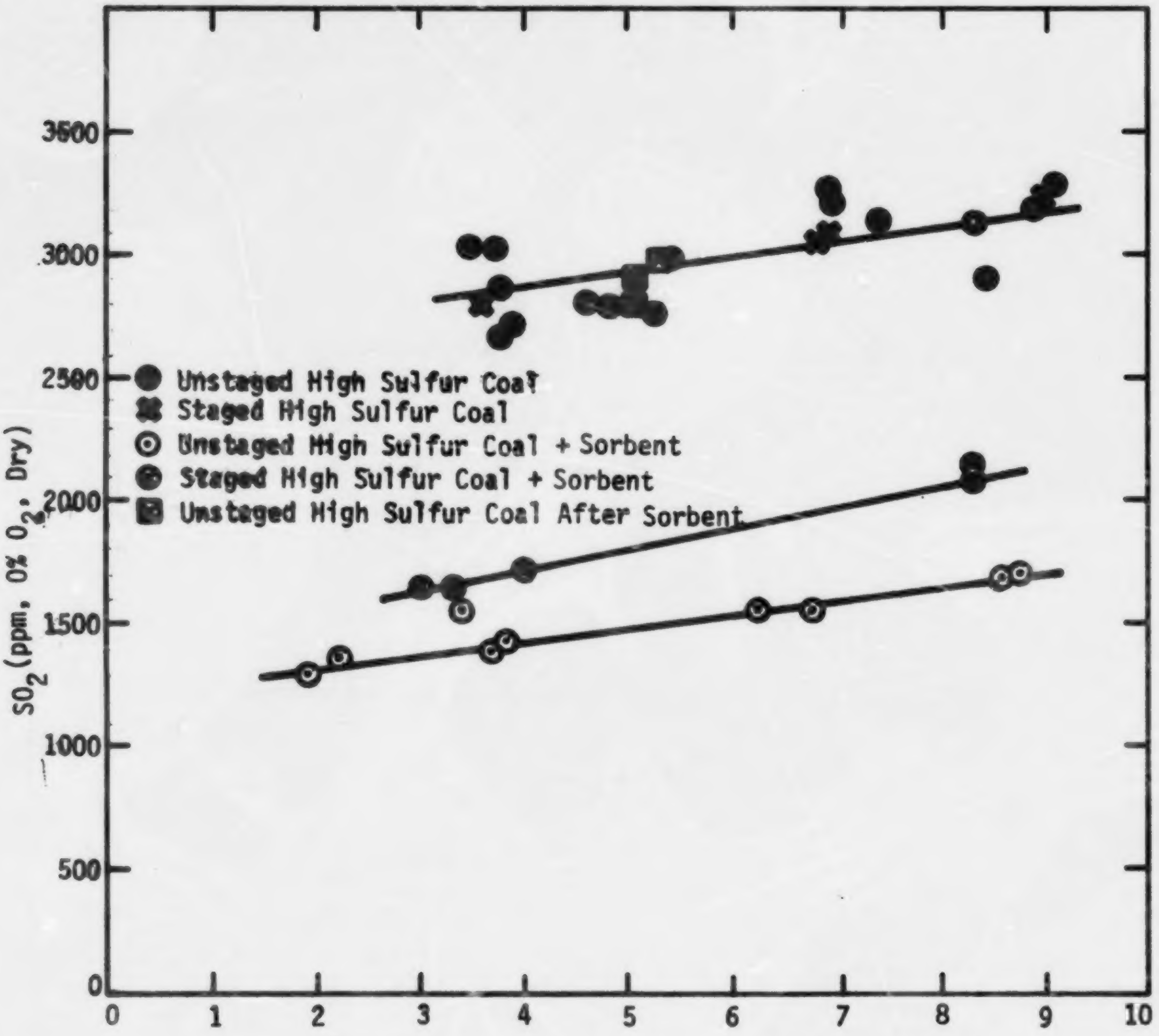


Figure 13. The Effect of the Addition of Limestone to the Western Kentucky Coal Prior to Pulverization on SO$_2$ Emissions (Ca/S = 1.0).

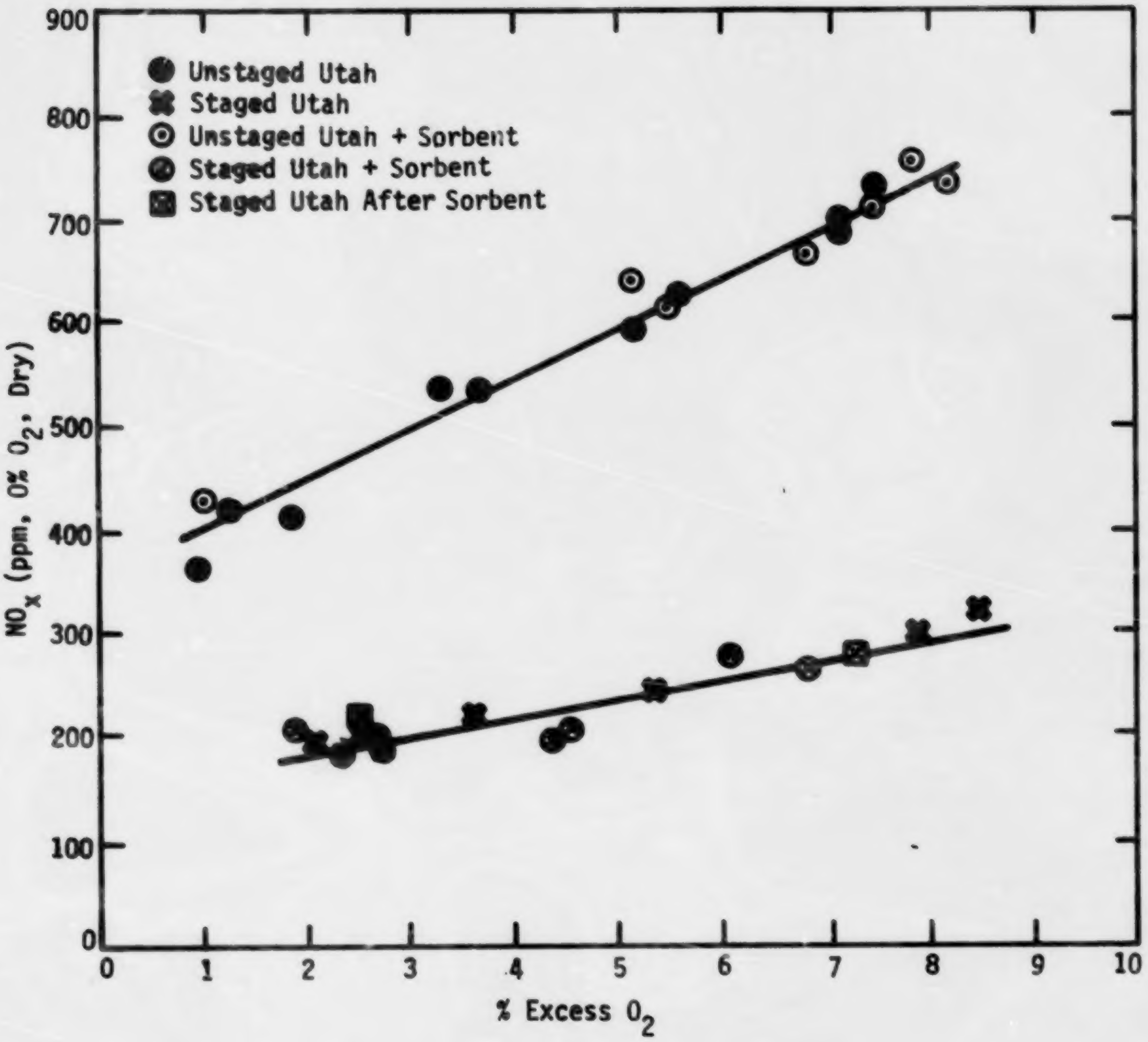


Figure 14. The Effect of Sorbent on NO$_x$ Emissions (Utah Coal Ca/S = 1).

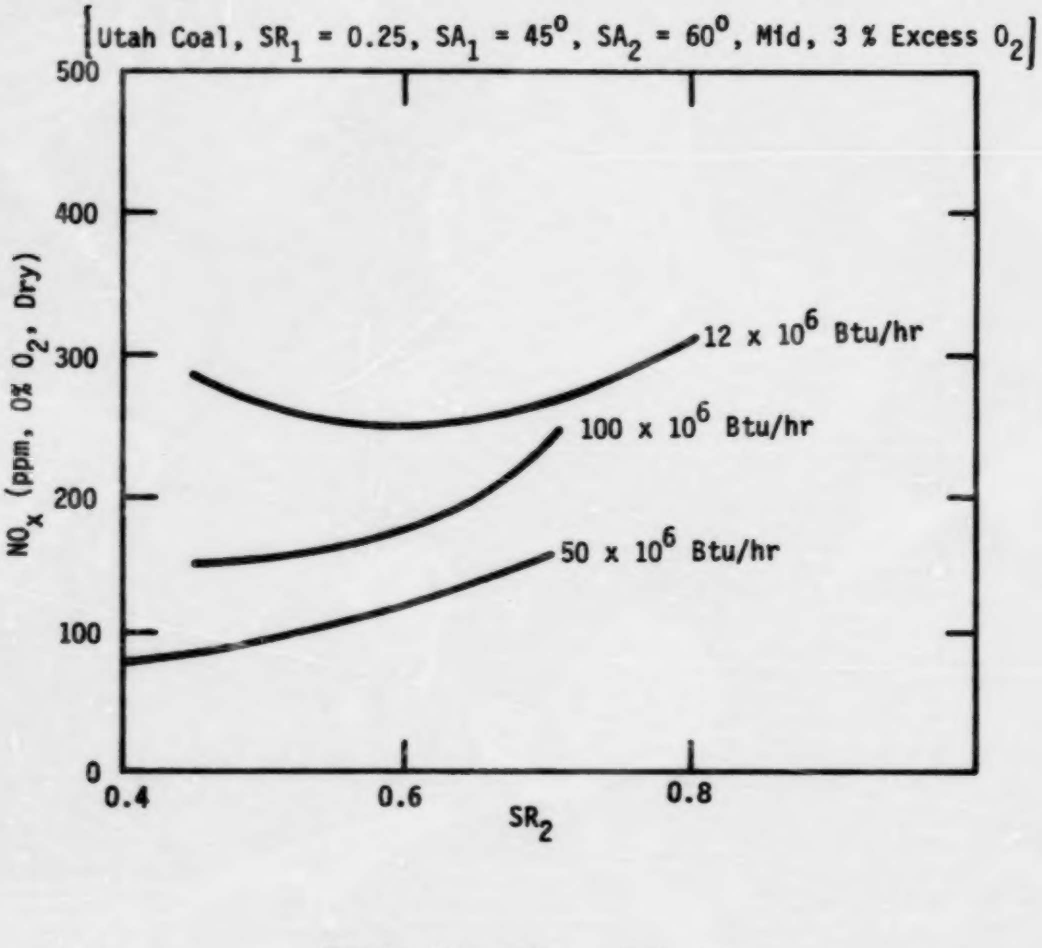


Figure 15. Effect of Scale.

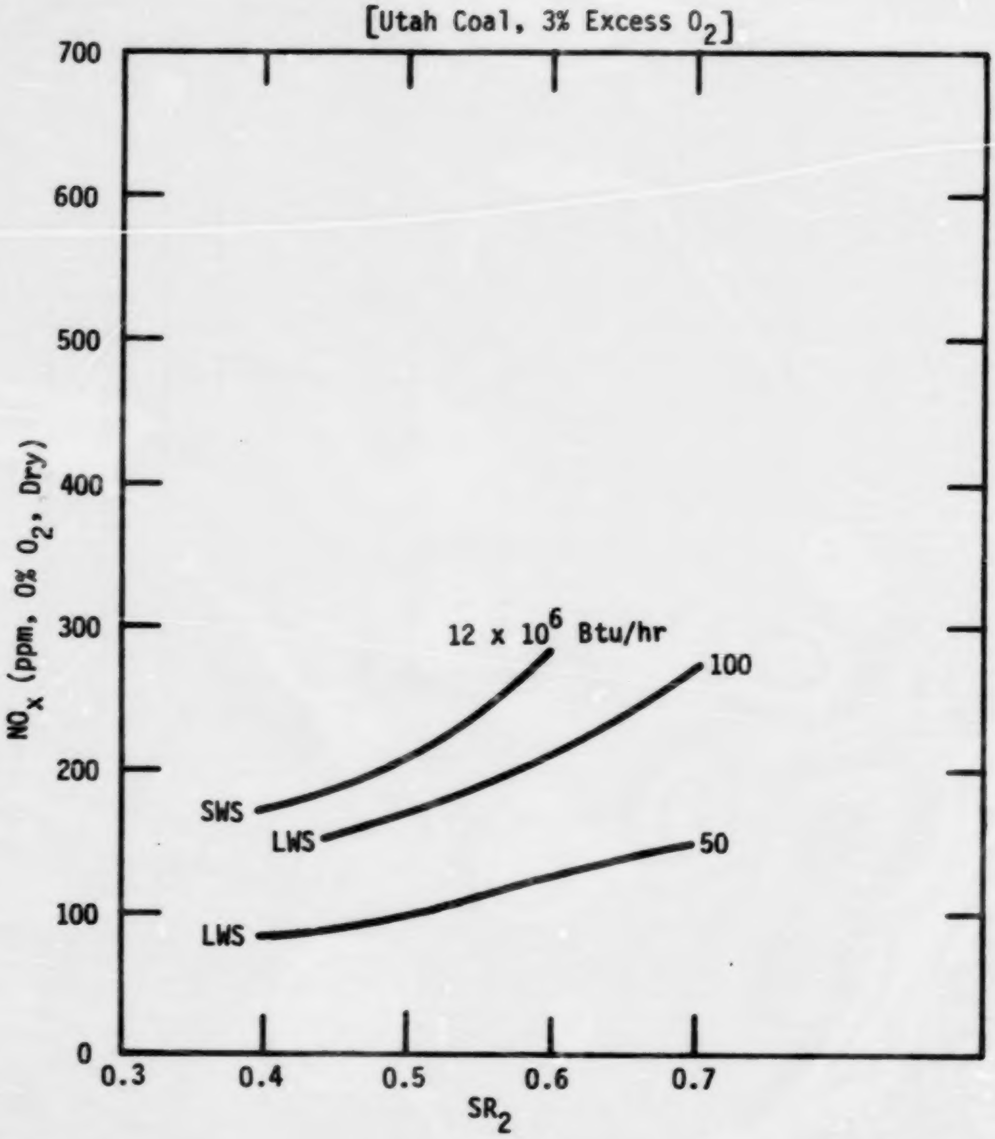


Figure 16. Performance at Optimum Configuration.

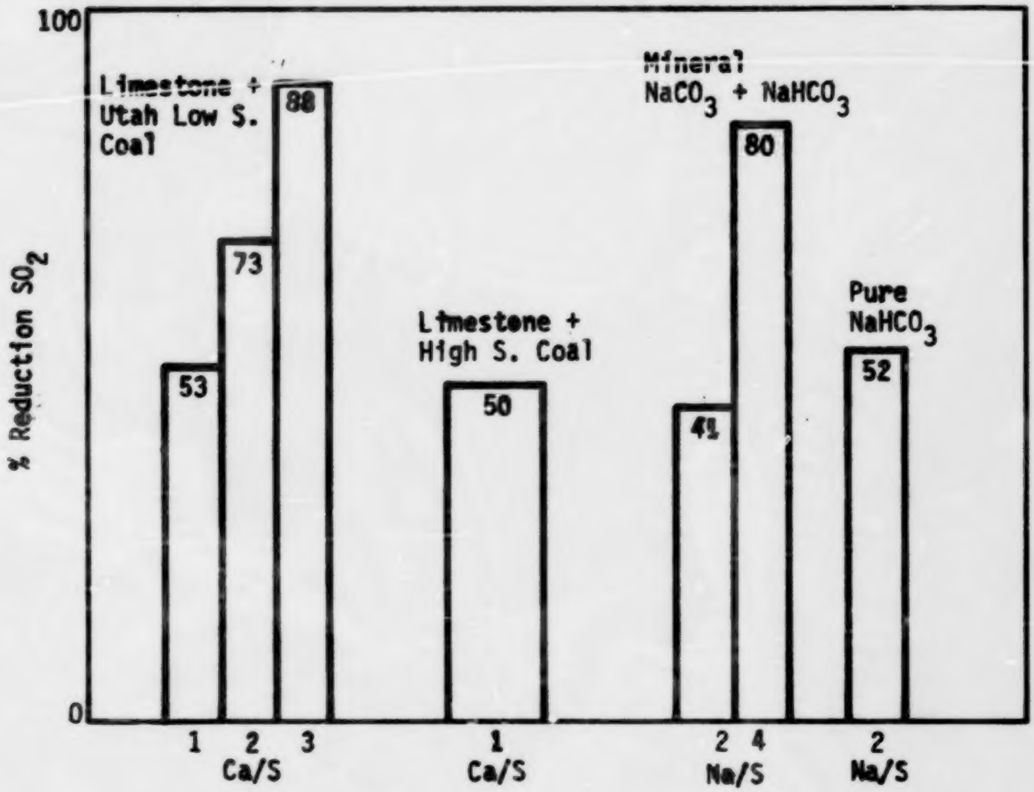


Figure 17. Summary of Sulfur Capture Results Using Various Sorbents and Molar Ratios.

TABLE I. COAL COMPOSITION

	UTAH	W. VIRGINIA	W. KENTUCKY
Proximate Analysis, % (as received)			
Moisture	6.39	1.29	3.68
Volatile	38.89	31.01	38.19
Ash	7.4	13.76	17.90
Fixed Carbon	47.32	53.94	40.23
Heating Value, Btu/lb	12,340	12,500	10,640
Ultimate Analysis, % (DAF)			
Carbon	79.45	83.92	77.57
Hydrogen	6.03	5.66	5.7
Nitrogen	1.44	1.55	1.63
Sulfur	0.74	2.06	3.8
Oxygen (by difference)	12.34	6.81	11.3

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ALTERNATE FUELS AND LOW NO_X TANGENTIAL BURNER DEVELOPMENT PROGRAM

BY:

Richard A. Brown
Acurex Corporation
Energy & Environmental Division
Mountain View, California 94042

ABSTRACT

The EPA is continuing to explore control technology in the areas of alternate fuels, waste fuels and control of NO_X emissions from tangentially fired boilers in the government owned test facility located at Acurex Corporation.

Results from baseline and combustion control technology tests on coal oil mixtures show that in general NO_X emissions of coal oil mixtures fall between the NO_X emissions of the parent oil and coal. Tests of NO_X control techniques including staging and a low NO_X burner design showed varying degrees of control depending on the particular fuel combination.

Baseline tests on refuse derived fuels (RDF) fired either with pulverized coal or natural gas were determined. Emissions assessments made include NO_X, CO, particulate loading and size distribution, twelve trace metals and a cursory search for PCB and POMs. NO_X emissions decreased as the percent RDF increased even though the available fuel nitrogen increased. Particulate loadings from the RDF were concentrated in the less than 1 μ size fraction.

An extensive research program has been initiated to develop a low NO_X burner design for coal fired tangential boilers. The initial tasks consist of firing the pilot scale facility on natural gas, natural gas doped with Nitrogen species, char, char plus natural gas, and coal to ascertain the relative importance of the various flame regions, coal volatiles and nitrogen evolution. In addition, a water model of the pilot scale unit is being constructed to ascertain the mixing patterns of the pilot scale unit as compared to the full scale unit.

SECTION 1

INTRODUCTION

The EPA multiburner multifuel test facility is continuing to explore control technology for alternate fuels and waste fuels. In addition, an extensive research and development program has recently been initiated to control NO_X emissions from tangentially fired utility boilers. This paper will: (1) review the data from tests on coal-oil mixtures and cofiring of refuse-derived fuels, and (2) present the test plans and objectives for the NO_X tangential burner development program.

The EPA experimental multiburner, furnace facility (Figure 1) was developed to study NO_X control technology problems associated with large - scale utility and industrial boilers. Details on this facility design have been discussed in other papers (References 1 and 2).

The furnace fires from 293kw-thermal to 880kw-thermal (1 to 3 x 10^6 Btu/hr) depending on the fuel and heat release per unit volume being simulated. The facility may either be front-wall fired using one to five variable swirl block burners, or it may be corner-fired using four to eight tangentially fired burners patterned after Combustion Engineering's design. A horizontal extension configuration (Figure 2) with a single large variable swirl block burner was used to conduct the coal-oil mixture tests. Radiant section cooling was simulated by placing water cooling coils on the inside circumference of the refractory tunnel. A convective section quenched the flue gases at the appropriate residence time.

The standard gaseous emissions (NO, CO, CO_2, O_2, SO_2) were continuously monitored throughout the test program. Particulates were obtained using a high volume EPA method 5 stack sampler; trace metals and organics sampling was obtained using the Source Assessment Sampling System (SASS) (Reference 3).

Coal-Oil Mixture Emissions

In many industrial and utility boilers, conversion to coal or partial coal could be accelerated if only minor modification to the boiler were required. Therefore, there is a growing interest in firing a mixture of coal and fuel oil in existing units.

It is now necessary to determine if current control technology for coal combustion is applicable to coal-oil systems or if further work is needed to ensure that pollution standards can be met.

The coal-oil mixtures examined were prepared from parent fuels which represent a broad range of fuel compositions. The compositions of the parent oils, coals, and coal-oil mixtures are listed in Table I. The coals, pulverized to 70 percent 200 mesh, were blended with the fuel oils and a suspension additive supplied by Carbonoyl Company that constituted 3.75 percent by weight of the mixtures. The mixtures were heated, thoroughly agitated by a variable speed rotary pump, and then delivered to the burner nozzle through heat traced lines.

The two nozzle types used were an air atomized combustion swirl Delavan Nozzle and an air atomized Sonicore Nozzle. Both of these nozzles underwent erosion during the tests. The Delavan 440 hardened stainless steel nozzle lasted approximately 3 to 4 hours on a coal-oil mixture of 30 percent coal until significant erosion produced an unstable flame. The Sonicore nozzle with a stellite tip lasted about 8 to 12 hours until performance deteriorated. Other operational problems included the rapid deterioration of pump seals and the gradual buildup and plugging of lines in the delivery system.

Figure 3 illustrates the results of the baseline emission tests. The NO levels for the Chevron-based fuels fall in an intermediate range between the parent fuels, while the data for the Amerada base mixtures are closer to the parent oil. This difference may be caused by sulfur in the fuel, atomization characteristics, and how the particular oil and coal volatilize.

At this point there is insufficient data to determine which mechanism is causing this effect; however, not all fuel combinations behave in the same manner.

In this study, established combustion control technology for pulverized fuel was applied to the coal-oil mixture, including staging the combustion air, burner air distribution or "low NO_X burner" configurations and combined staging and low NO_X burner design. Only the combined low NO_X and staging tests will be reported here. The low NO_X burner involves axial injection of tertiary air at the periphery of the burner diameter.

The curves in Figure 4 compare the results of applying burner air distribution plus staging to straight burner air distribution. The purpose of this comparision was to evaluate the mixture responses with an enriched flame zone. For the western Kentucky/Amerada mixture, further enriching the flame zone resulted in higher NO levels. This result may further illustrate the response of the Amerada high sulfur parent oil to fuel-rich conditions. The Montana/Chevron mixture results validate that each mixture responded favorably to the air distribution, but that the composition of each mixture leads to a unique emission curve.

The following conclusions can be drawn:

- NO emissions from coal-oil combustion are affected by the composition of the parent fuels which make up the mixture
- Present conventional control technology used for pulverized fuel combustion reduces NO emissions produced by coal-oil mixture combustion
- Coal-oil mixture flames do not react consistently to some forms of control technology, implying that the chemical properties of the fuel and the physical processes which take place during combustion are both important
- Coal-oil mixture combustion is different from either pulverized coal or residual oil combustion. Therefore, predictions of NO emissions based on emission levels of the parent fuels often will not be valid

In order to analyze and understand coal-oil mixture combustion, better understanding of the combustion processes of each parent fuel must be obtained. Also, the combustion of coal-oil mixture must be examined to determine if it is merely a combination of the two individual processes or instead is a completely different physical and chemical phenomena.

Future work should examine the role of fuel-bound nitrogen utilizing flue gas recirculation, nitrogen evolution studies of the parent oils, and the effect each fuel exerts on the other, such as shielding or physical separation in the droplets.

SECTION 2

REFUSE-DERIVED FUEL TESTING

There is condiderable heating value (4000 to 7000 Btu/lbm) associated with municipal solid waste. If this resource could be used in steam boilers rather than lost by incineration, a significant energy resource would be tapped.

Research studies have included using heat recovery incinerators, spreader type stokers and suspension firing in large electric utility boilers. The EPA has supported experiments in cofiring the refuse-derived fuel (RDF) in full scale boilers in St. Louis, Missouri, Ames, Iowa, and Columbus, Ohio (References 4 through 7).

Although these full scale experiments are providing useful data, problems associated with the many varieties of RDF need to be studied. Because the refuse comes from local municipalities, there can be significant variations in the combustion and environmental characteristics of the fuel from season to season or from locale to locale.

There is little published data on the emissions from RDF when cofired with other fuels. Kilgroe (Reference 8) reported that the St. Louis demonstration site produced a moderate increase in chloride emissions but that the RDF did not significantly affect the SO_2 or NO_X emissions. Little information is available on the amount of trace metals and organics or the nature of the particulates. The work performed here provides the initial data base to answer environmental questions on four RDF's.

The refuse-derived fuel tests were conducted in the main firebox in the tangentially fired mode. First, a feed system (Figure 5) was designed to control and measure from 10 to 60 lbs/hr of varied refuse-derived materials. RDF is delivered to the upper part of two diagonally opposed corner-fired burners. Natural gas or coal is also delivered to these burners and to the other two burners. The RDF feed system consists of a rotating drum hopper which deposits the material on a conveyor belt. The conveyor delivers the material to a vertical downcomer, where it is pushed through by a blast of air. Additional air at the junction of the vertical downcomer and horizontal feed tube conveys the RDF into the furnace through a horizontal water-cooled feed tube. The RDF feedrate is controlled by a variable-speed drive on the feed belt; the drum is maintained at constant optimum speed to keep the feed belt full.

The delivery tube is sized to prevent blockage while minimizing the transport air. This sizing is critical for a small-scale facility where the minimum pipe size is governed by the maximum particle size and the minimum conveyance air needed to keep the material suspended. The received RDF material was shredded from a nominal 2 to 4 inches down to 1 to 2 inches using a conventional garden shredder to reduce the feed tube diameter and transport air flow to an acceptable level.

The test program determined the gaseious, particulate trace metal and organic emissions of refuse-derived fuel from San Diego, California; Richmond, California; the Americology Facility in Milwaukee, Wisconsin; and Ames, Iowa.

All of these materials had gone through metals and glass separation and a primary shredding. Table II shows the composition and heating value for each fuel type.

Figure 6 shows the effect of NO versus excess air for the four fuels at 20 percent RDF and 80 percent natural gas. Although the NO levels are not particularly high, there was a definite difference between the fuels. The NO also increases with both excess air and increases in RDF. Also, when the percent RDF is increased and cofired with coal, the NO levels decrease (Figure 7) while total fuel nitrogen increases. This is possibly the result of enriched fuel jets at the coal-refuse injection guns. Except at very low excess air (5 percent) CO levels were always less than 100 ppm.

Results from the particulate, trace metal, and organics sampling also provide some interesting preliminary information of RDF emissions. Table III shows the results of particulate concentrations in the various size cuts for four RDF materials cofired with natural gas. Although the total particulate quantity was quite low in all cases, the majority of particles were smaller than 1 μ and collected only on the filter. Although the particulate may be rather friable and break up in the sampling equipment during collection, it may eventually end up in the respirable size range.

Table IV shows particulate loading in the same size cuts for two levels of Richmond RDF cofired with coal and for coal alone. With the substitution of RDF, the total grain loadings decreased with increasing RDF. However, in both cases, adding RDF increased the percent of material in the 1 μ size cut over coal alone. Thus, it appears that adding RDF may increase the grain loading in size cuts less than 1 μ. This result could produce problems for flyash collection equipment. Percent combustibles in the particulate were generally less than 2 percent except when the excess air levels were 10 percent or less. This result also corresponds to generally low CO (< 100 ppm) and unburned hydrocarbon levels.

Table V lists the total trace metals in micrograms/Btu found in the particulates and the condensable vapor for: 1) coal only, 2) coal plus 10 percent RDF, and 3) gas plus 10 percent RDF. Increases in trace metal concentrations varied among the three tests. In the coal only test, the lead concentration was exceptionally high. In addition, no correlation was found as the percent of RDF was increased.

It is difficult to draw any conclusions from this trace metal data. Several factors may be contributing to the data variability:

- The RDF material is nonhomogeneous and will vary from minute to minute, hour to hour, and season to season
- Metals from the furnace and sampling system could contribute to the trace metal loadings

- Hold up in the convective section
- Analytical error

These factors indicate the need for a broader data base to draw meaningful conclusions on trace metal concentration when cofiring RDF with other fuels. This data will contribute to that base, but a larger sample of data is needed to statistically determine real trace metal effects.

In addition to trace metals, a limited search for organics in terms of (PNA or PCB's) was undertaken. A portion of the particulate and the XAD-2 organic section resin of the SASS train were analyzed by liquid chromatography according to EPA Level 1 procedures (Reference 9). Of the material divided into the standard seven cuts, only cuts two and three were expected to contain PNA and PCB. Therefore, these two fractions were combined for a single GC/MS analysis. Five out of nine tests where organic samples were taken contained no detectable compounds. Test conditions, and the PNA found in the remaining samples, are listed in Table VII. No PCB was found in any of the test samples.

Little organic material, combustible CO, and unburned hydrocarbons were found in the particulate and gaseous streams. It has been reported (Reference 8) that significant quantities of unburned material have been found in full-scale tests. These pilot scale tests have higher combustion efficiency over full-scale tests possibly because of the additional shredding and/or hot refractory walls providing an improved ignition source.

In summary, up to 30 percent RDF may be cofired in a subscale test facility without experiencing a reduction in combustion efficiency. Additional studies are necessary to determine how this technology can be implemented in a full-scale facility using the same degree of efficiency but a higher RDF percentage. Furthermore, the flame's heat transfer characteristics must be clearly defined to determine the effect on the boiler steamside or to design a boiler specifically for cofiring RDF. Finally, more data is needed to statistically determine the trace metal and organic makeup of RDF cofired boilers emissions.

SECTION 3

LOW NO_X TANGENTIAL BURNER DEVELOPMENT

INTRODUCTION

The RDF work is being followed by development of a low NO_X tangential burner for utility boilers. The following sections describe the background and program plans for this work.

Tangential coal-fired boilers produce approximately 10 percent of all stationary source NO_X emissions and consume, in Btu's, approximately 9 percent of all fuel used in stationary sources. Reducing tangentially coal-fired boiler NO_X emissions is necessary to maintain ambient air quality in the United States. The need to address the long-term capabilities of the corner-fired boiler is becoming more apparent as recent developments in low NO_X burners for front wall-fired boilers have reached the 125 ppm range (Reference 10).

Therefore, the EPA has contracted with Acurex Corporation to conduct a 31-month program to develop a low NO_X burner concept for tangentially fired boilers. The two principle goals of this program are to:

- develop a better understanding of processes controlling NO_X formation during combustion of pulverized coal in tangentially fired furnaces
- develop low (50 to 100 ppm) NO_X combustion concepts for retrofitting or new designs of tangentially fired boilers

Figure 8 shows the flow patterns typically present in the tangentially fired system. Air and fuel are distributed in a nonswirling slow mix character through registers located in vertical orientation at each of the four corners. Generally there are three to five fuel register levels. Fuel ignition is provided by impingement of hot laterally adjacent streams and large-scale internal recirculation of combusted gases. Thus, the ignition and combustion of each corner jet serves to ignite and promote burning in the downstream adjacent jet. A large-scale vortex is formed by the tangential nature of the air and fuel injection. This vortex motion promotes mixing of fuel-rich regions, internal recirculation flow patterns, and the slow-mix nature of the jets should inherently make the tangentially fired system low in NO_x production. The pilot-scale facility models most of the significant parameters of the tangential system. For example, the fuel and air are distributed in a manner similar to the full-scale system. The bulk residence time and heat transfer rates are also maintained. However, the residence time between adjacent jets is condiderably different than in the full-scale system, and fuel is introduced only at one or two levels.

Although there is a three-dimensional aspect to the tangential boiler flow patterns, our primary concern will be the flows encountered at a single elevation. Figure 9 and the following paragraphs define three regions in a tangentially fired boiler:

- Near burner-early mixing
- Intermediate jet flame
- Recirculating fireball

Near Burner-Early Mixing Region

In this region, flow is predominantly an axial jet that entrains air and small amounts of flue gas. The region consists of approximately the first five flow path jet diameters where significant coal devolatilization occurs, including the flame's ignition region. It is believed that a high peak NO is formed early in this region.

Intermediate Zone

In this region, consisting of five to perhaps 30 fuel jet diameters, the remaining air is mixed with the fuel, the majority of the fuel is burned, and considerable flue products are entrained. In this region, one side of the flame interacts with the fireball, and the opposite side interacts with the boiler wall. Locally rich combustion zones which have the potential to reduce entrained burnt gas NO_X by flame processing can exist here.

Fireball

The fireball consists of the recirculating zone in the firebox center. It is believed that this zone consists mostly of flue gas products and regions where char is burned out. However, it is not known at this time if any additional NO is formed here, or if NO formed early is reduced.

The proposed research program focuses on the physical and chemical processes associated with NO_X formation in the near, intermediate and fireball zones.

APPROACH

The proposed approach is deiplayed in Table VII.

Task A -- Tangentially Fired System Definition and Evaluation

The primary goal of Task A is to define the phenomena which control the formation and reduction of both fuel and thermal NO in a classical tangentially fired boiler. This task will isolate the critical chemical and physical processes (e.g., early mixing, flame shielding, devolatization, etc.) and establish the design parameters effect on these processes. Task A will also investigate the uniqueness of tangential firing and attempt to definitively show why such a system generally has lower NO_X emissions than wall-fired units. The majority of this work will be done in the existing pilot-scale facility. In each region the importance of the volatiles and char burnout will be investigated by doping char, natural gas flames, and natural gas plus char with nitrogen and sulfur compounds.

We will also focus on hot sampling for NO and flame-flame interaction studies. It is possible that NO formed in one flame can be reduced by passing through an adjacent flame. Figure 10 shows parameters that will be investigated, including the intersection point of the two flames, X, and the intersection angle over a range of fuel richness in each flame.

Therefore, these subtasks will help focus subsequent tests on the those chemical/physical processes offering the greatest potential for NO_X reduction.

At the completion of Task A, sufficient understanding and information on tangential system NO_X formation processes will be available to permit the design, construction, and test of specialized low NO_X burner/firebox subcomponent hardware.

Task B -- Optimization of Near Burner and Intermediate Zone NO_X Levels

The primary objective of this task is to follow through on the guidance provided by Task A; and to design, construct, and test (in subscale), low NO_X subcomponent concepts of near and intermediate zones. Sufficient flexibility will be incorporated into the hardware to define optimal low NO_X conditions for both the near burner and intermediate field zones. Parameters optimized during these tests will be air and flue gas distribution, and mixing and temperature history, or local cooling rates. The B tasks will utilize a new versatile burner which fires into the horizontal furnace extension. In these initial tasks, the near burner early mixing zone oxygen, flue gas availability and temperature/cooling rate history will be optimized for low NO_X. Optimal and off-optimal near burner configurations will then be tested with intermediate zone air and flue gas distribution, and wall cooling. For these tests, air and flue gas introduction ports, and wall cooling panels will be incorporated into the horizontal firebox appendage.

Optimal near and intermediate zone low NO_X concepts will emerge from the Task B tests. These concepts will be applied in the pilot-scale tangentially fired tests carried out in Task C.

Task C -- Optimization of Coal-Fired Tangential System Low NO_X Concepts

The primary objective of this task is to define and demonstrate in pilot scale, low NO_X tangentially fired systems for several coal types. This task will adapt the low NO_X subcomponent concepts developed in Task B into the tangential firebox and optimize the complete system for low NO_X. The system will be optimized for each coal type tested.

The optimized low NO_X tangential system concept will be demonstrated on a single characteristic coal. Sufficient parameter variation will be built into the hardware to optimize the system for the characteristic coal used in this task or any other commonly used coal. Then the low NO_X concept will be optimized for several additional coal types.

Fireball Simulation Study

Throughout the 31-month program, a background study will determine how to best simulate a tangentially fired system in subscale. The study will identify and quantify the following parameters important to modeling:

- Mixing rates
- Temperature/time history
- Fuel type and size
- Burner firebox geometry

Previous hot and cold flow studies on tangential systems, such as those by Juniper (Reference 11) will be studied.

To assess the overall flow simulation of the pilot scale versus the full scale, a water model of each system is being constructed. Flow patterns will be observed using a dye injection technique and recorded by still and motion pictures. To assess the mixing patterns for the new concept in the tangential mode, models will also be made of the low NO_X burner design concepts.

CONCLUSION

Completion of all proposed program tasks will result in a pilot-scale demonstration of a low NO_X tangentially fired system for several coal types.

Following the program's completion, research will be conducted to either: 1) demonstrate the low NO_X concept in larger scale with possibly a greater variety of fuels, or 2) carry out additional subscale tests. This will eventually lead to an optimal low NO_X full-scale tangentially fired system capable of firing several coal types.

SECTION 4

SUMMARY

The paper presented three facets of EPA's program on emission characterization and control of alternate waste and conventional fuels. First the facility simulated the combustion characteristics of a package boiler to test emission characteristics of coal oil mixtures. Different fuel combinations of a coal-oil mixture responded in a unique manner to conventional control technology. In addition, many operational problems (pumping characteristics, pump seal wear, and nozzle erosion) were discovered.

Tests were also conducted to determine the feasibility of subscale evaluation of cofiring refuse-derived fuels. A unique feed system was developed to deliver a variety of RDFs from 10 to 60 lbs/hr. However, it was found that the test furnace was even more efficient in achieving complete combustion than full-scale units.

Tests showed slight increases in NO and SO_2 emissions over natural gas but demonstrated a reduction in these levels when cofired with pulverized coal. When cofired with natural gas, the particualte was found concentrated in less than a 1 μ range. The trace metal analysis showed no conclusive trends. Few PNA organics emissions and no PCB materials were found.

The program plan to develop a low NO_X tangential burner was presented. This plan includes tests to: 1) determine formation and destruction of NO in current designs; 2) optimize early and intermediate zone environmental conditions, and 3) optimize low NO_X concepts in the pilot-scale facility. A water modeling study will also be employed to study the mixing patterns in the pilot-scale and full-scale systems.

SECTION 5

REFERENCES

1. Brown, R. A. et al. Pilot Scale Investigation of Combustion Modification Techniques for NO_X Control in Industrial and Utility Boilers. EPA-600/2-76-152b. Proceedings of the Stationary Source Combustion Symposium, Volume II, June 1976.

2. Brown, R. A. et al, Investigation of Staging Parameters for NO_X Control in Both Wall and Tangentially Coal-Fired Boilers. EPA-600/7-77-073C. Proceedings of the Second Stationary Source Combustion Symposium, Volume III, Stationary Engine, Industrial Process Combustion Systems, and Advanced Processes, July 1977.

3. Blake, D. Source Assessment System Design and Development, EPA 600/7-78-018, August 1977.

4. Vaughan, D. A. and Associates. Report of First Year Research on Environmental Effects of Utilizing Solid Waste as a Supplementary Powerplant Fuel, Battelle Columbus Ohio Laboratories, EPA Research Grant R-804008, June 1975.

5. Nydick S. E. and Hurley, J. R. Study Program to Investigate Use of Solid Waste as a Supplementary Fuel in Industrial Boilers, Thermo-Electron Corporation. EPA Contract No. 68-03-3005, January 1976.

6. Riley, B. T. Preliminary Assessment of the Feasibility of Utilizing Densified Refuse Derived fuel (DRDF) as a Supplementary Fuel for Stoker Fired Boilers, published report to EPA, 1975.

7. Vaughan, D. A., Krause, H. H., Hunt, J. F., Cover, P. W., Dickson, J. D., and Boyd, W. K. Environmental Effects of Utilizing Solid Waste as a Supplementary Powerplant Fuel. Seventh Quarterly Progress Report, EPA Research Grant 804008-02-1, 1975.

8. Kilgroe, J.D., Shannon, L.J., Gorman, P. Environmental Studies on the St. Louis Union Electirc Refuse Firing Demonstration.

9. IERL/RTP Procedures Manual: Level 1, Environmental Assessment, Second Edition. June 1976.

10. New Coal Burner May Reduce Nitrogen Dioxide Emission 80 to 85 percent. EPA/Environmental News Release, Office of Public Awareness (A-107), Washington, D.C., September 22, 1978

11. Juniper, L. A. Flame Measurements in a Brown Coal Fired Furnace, Combustion Institute European Symposium, Academic Press, 1973.

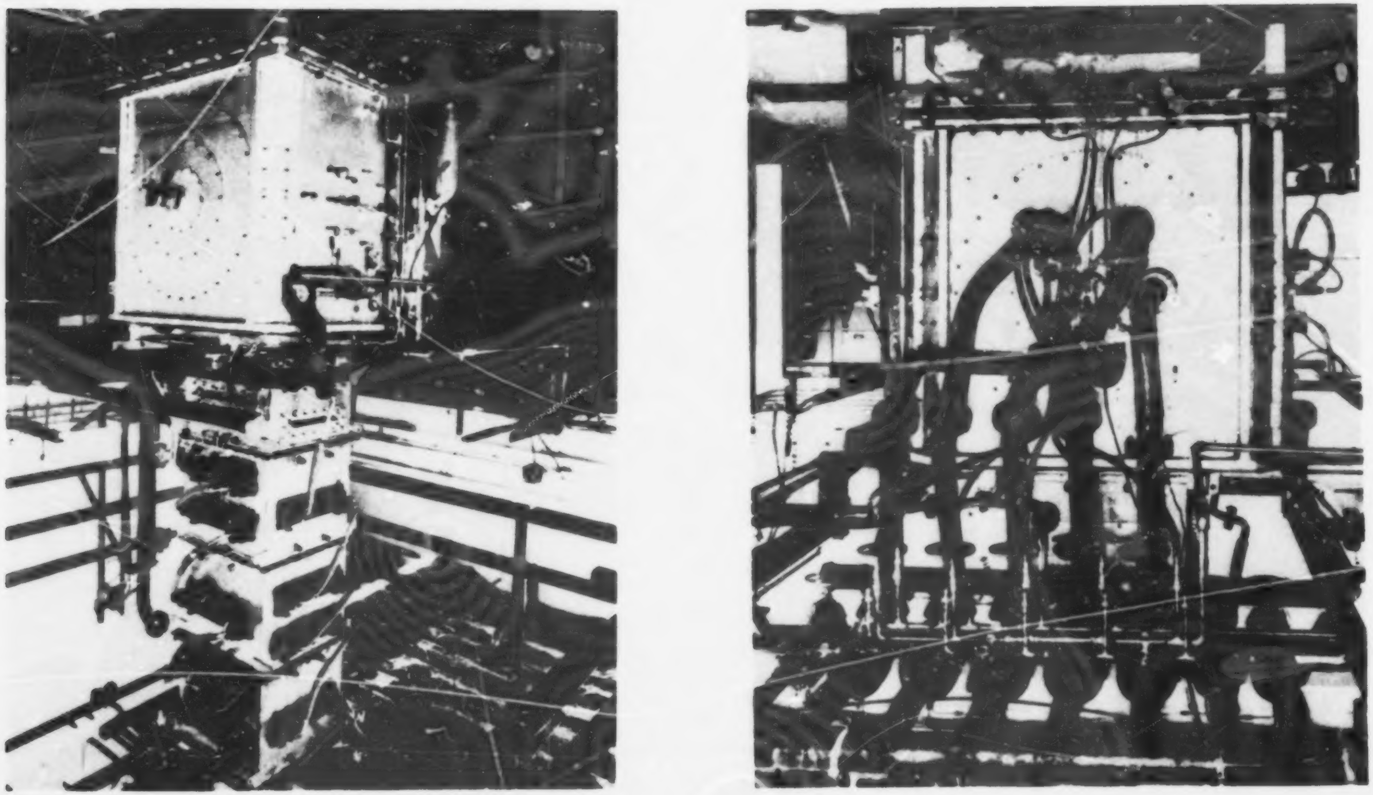

Figure 1. Photograph of experimental multiburner furnace.

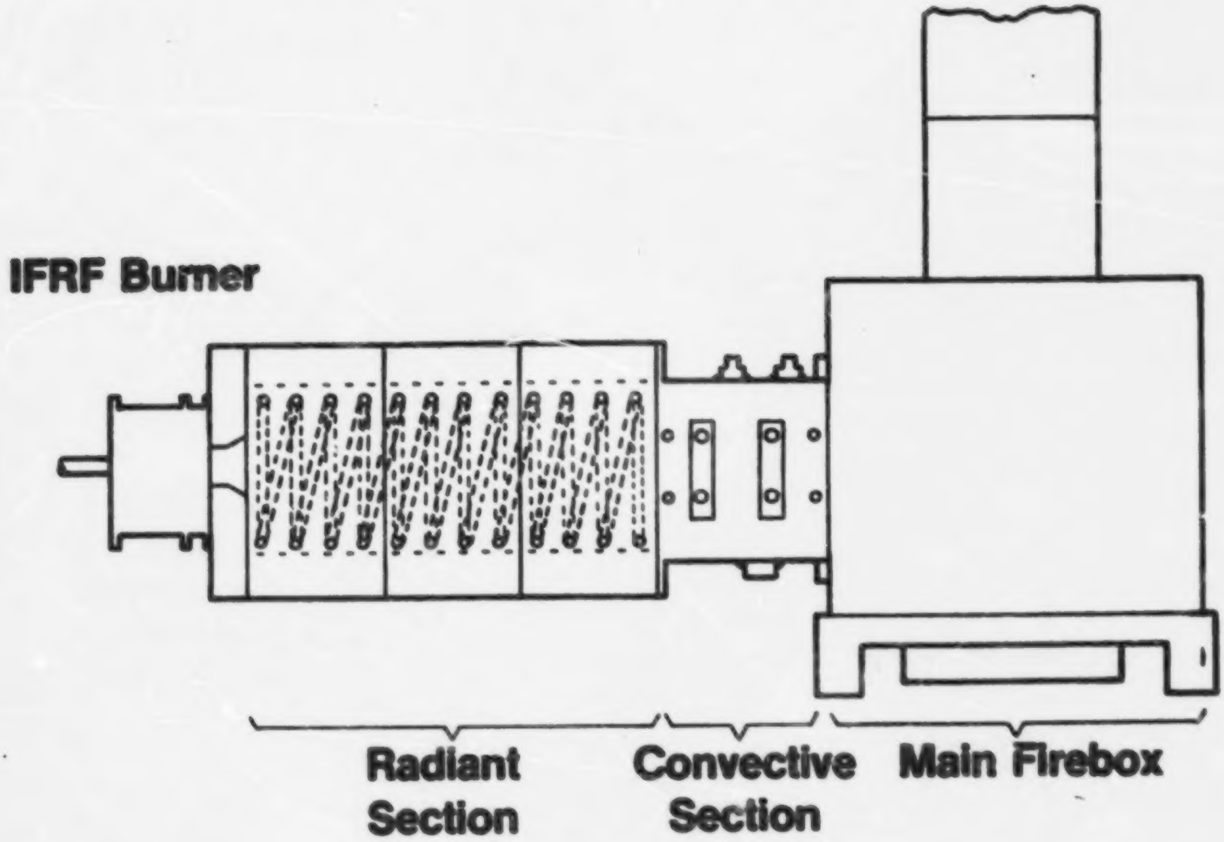
IFRF Burner
Radiant Section
Convective Section
Main Firebox

Figure 2. Package Boiler Configuration

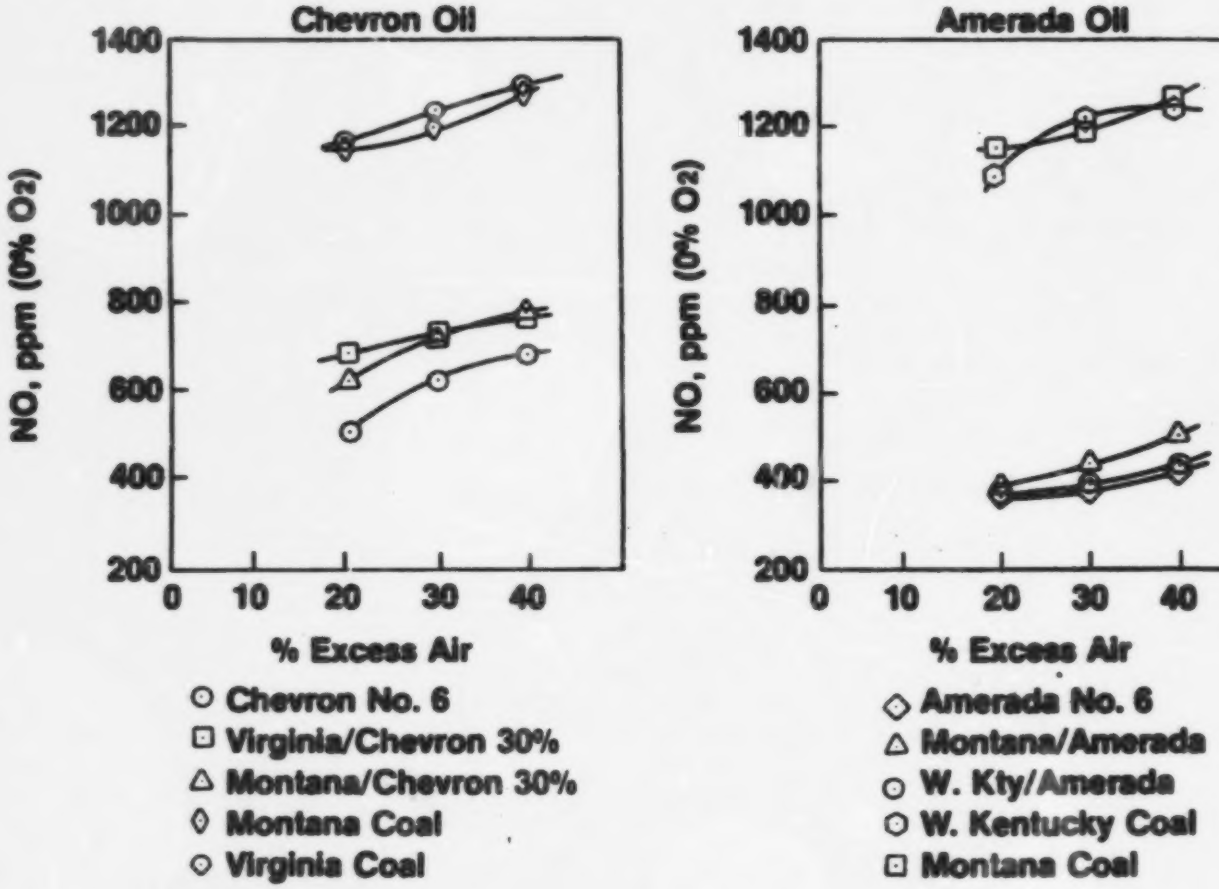

Figure 3. COM Baseline Emissions

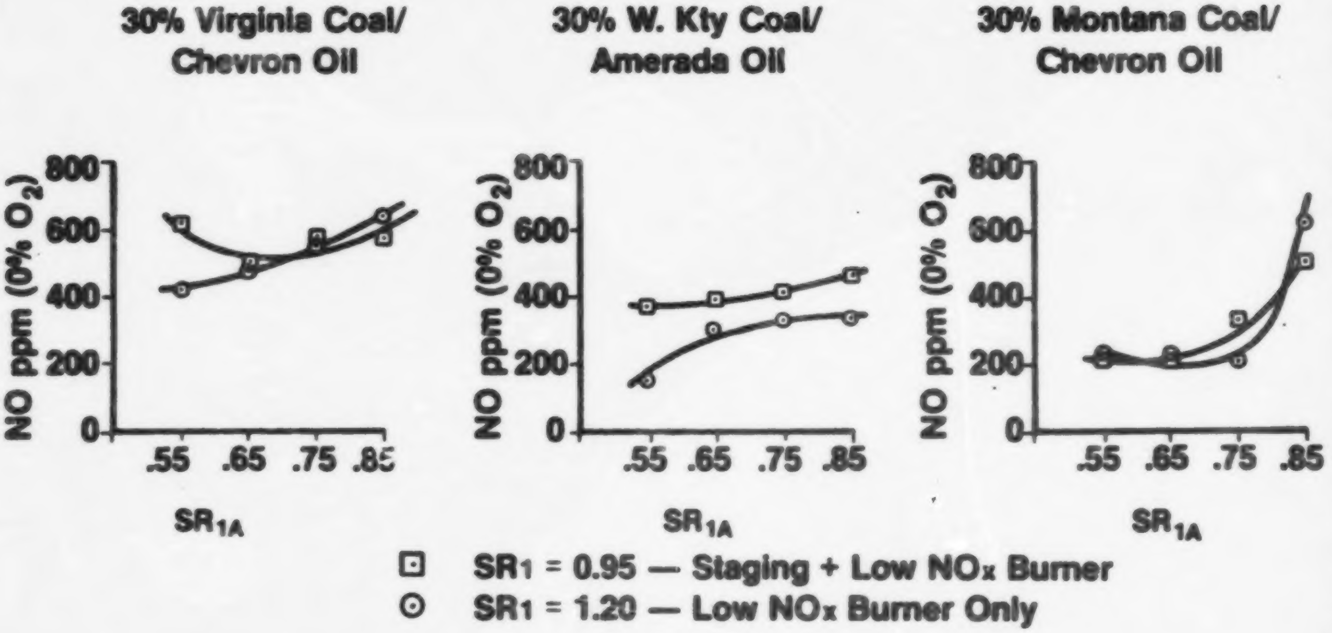

Figure 4. Combustion Modification Results

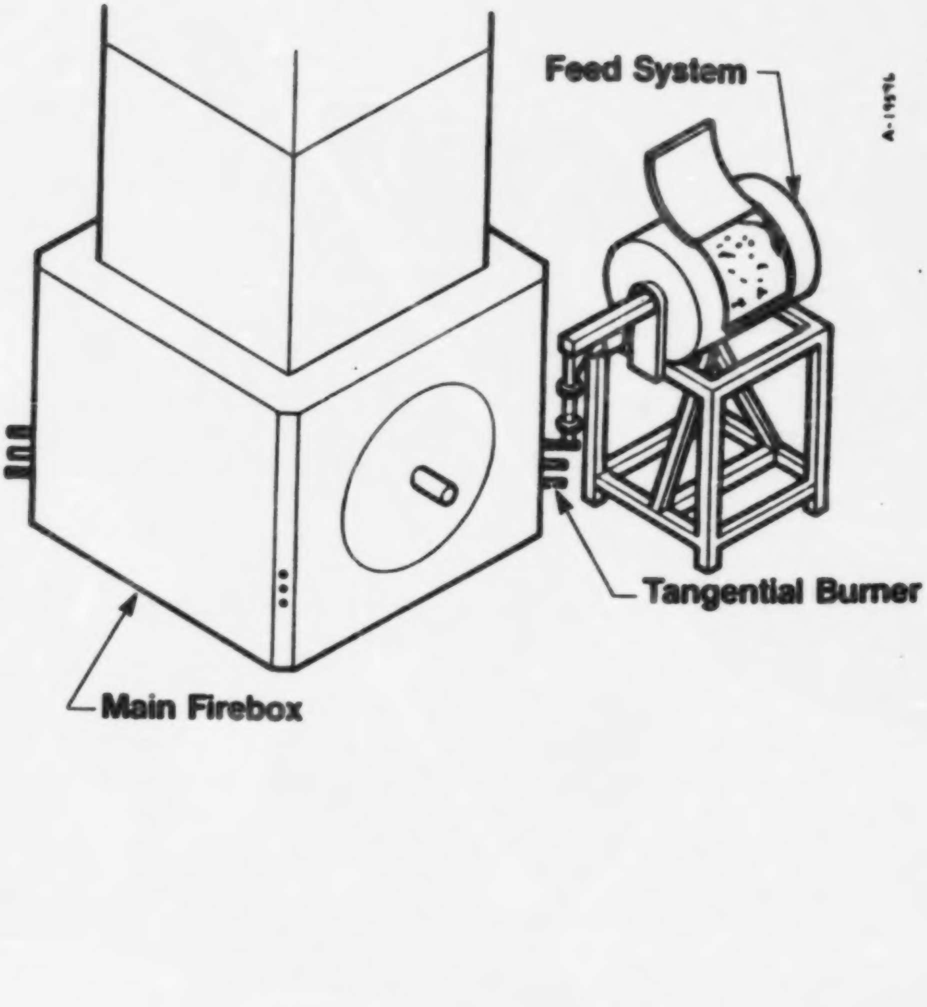
Feed System
A-19596
Tangential Burner
Main Firebox

Figure 5. RDF Feed System and Firebox

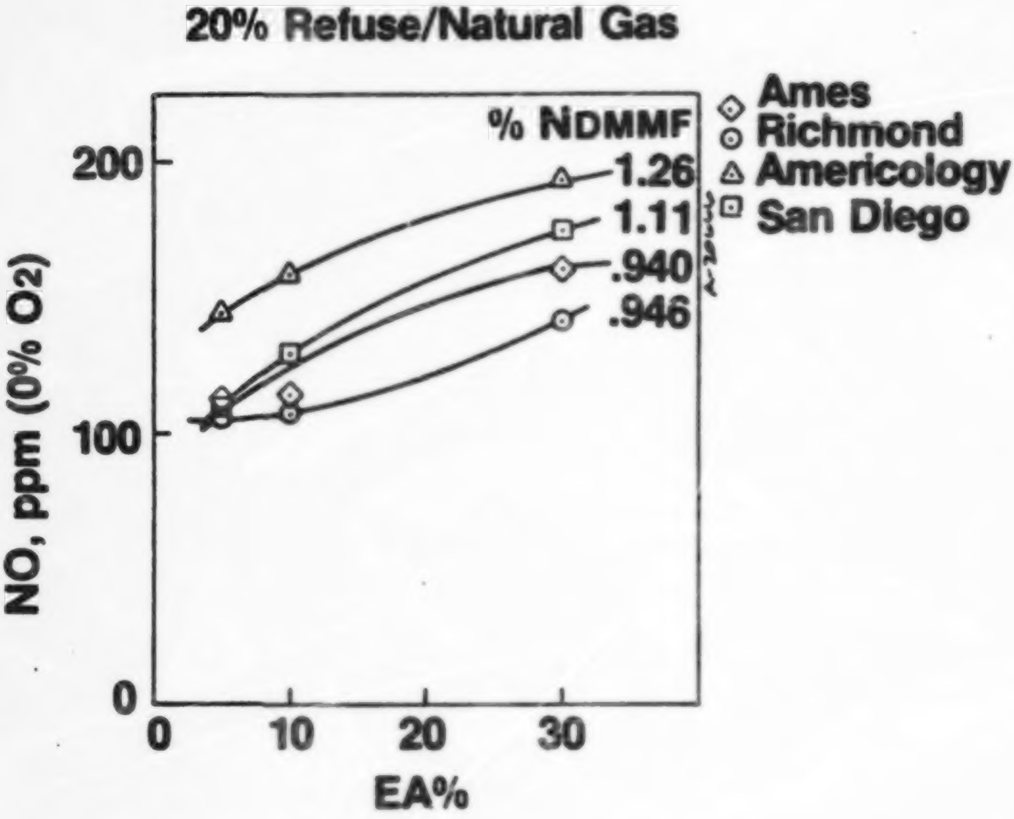

Figure 6. Baseline NO_X - Emissions - RDF & Gas

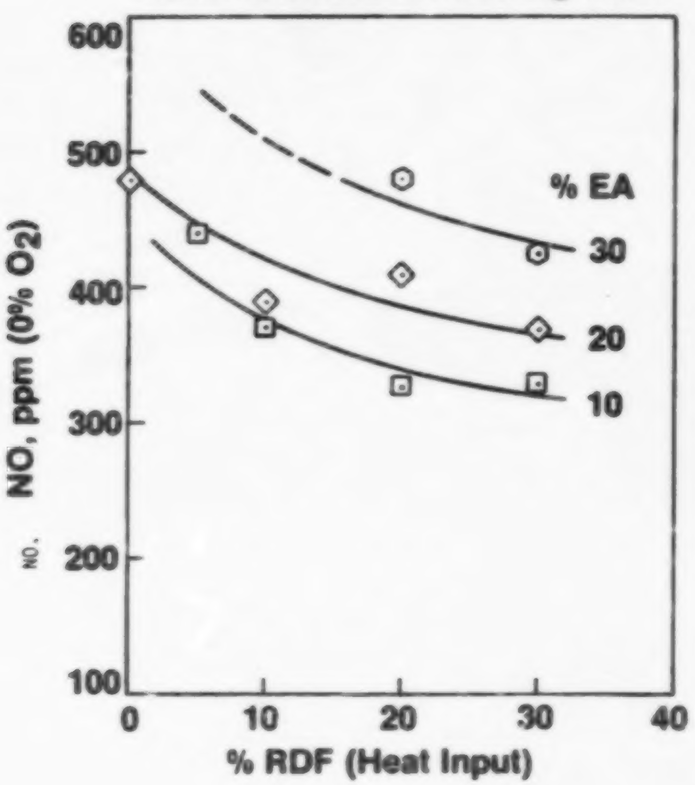

Figure 7. Effect of Percent RDF Coal & RDF

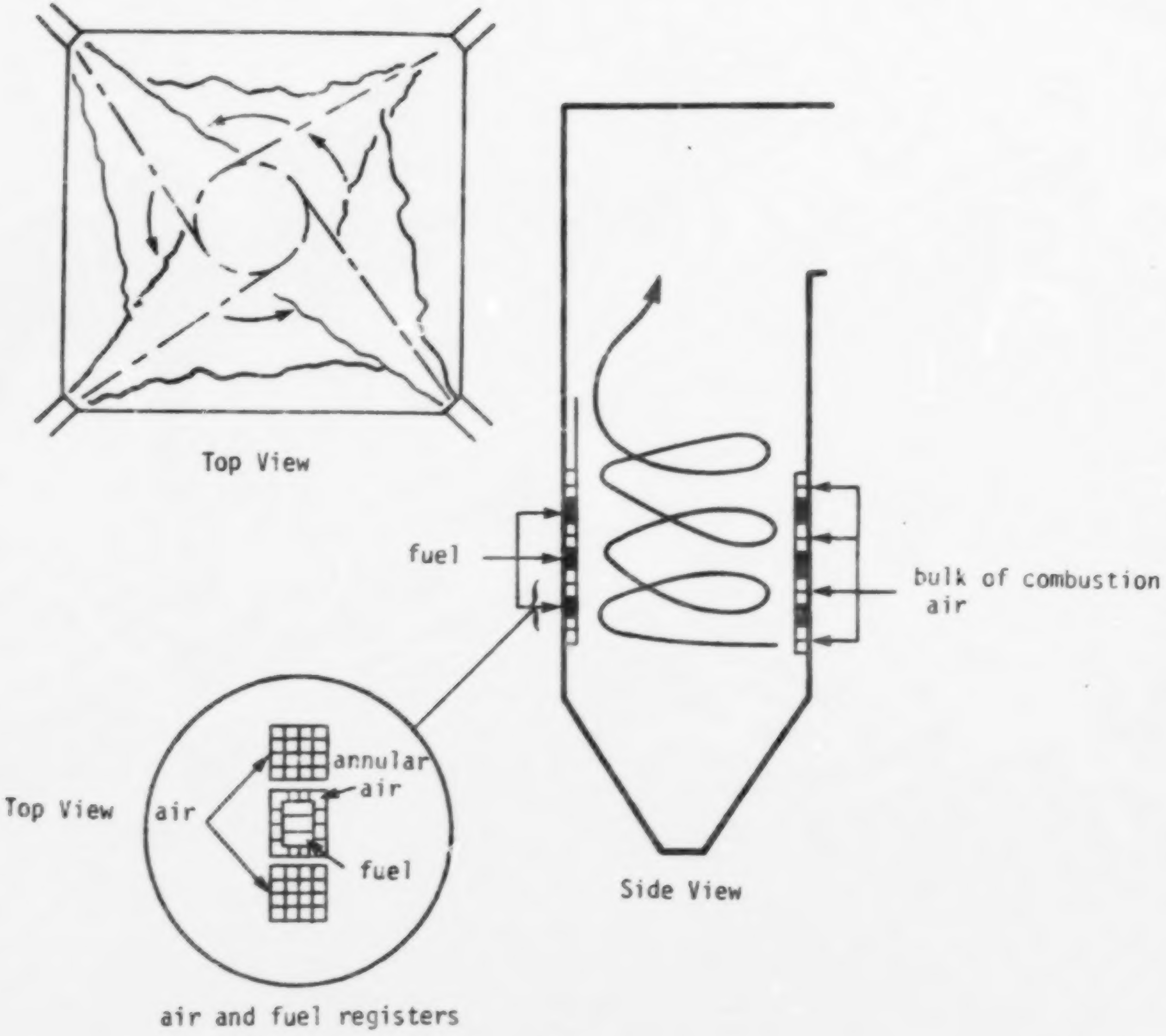
Top View
fuel
bulk of combustion air
annular air
Top View
air
fuel
Side View
air and fuel registers

Figure 8. Tangentially Fired System Flow Patterns

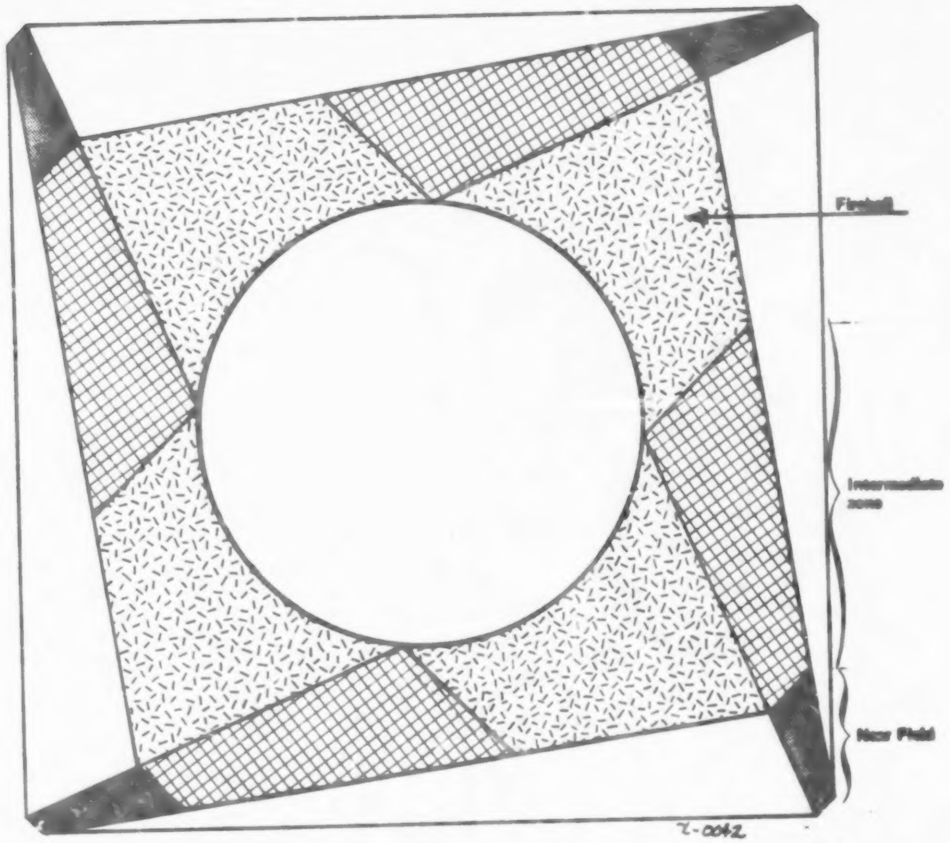
Fireball
Intermediate zone
Near Field
Z-0042

Figure 9. Tangential Burner Flame Regions

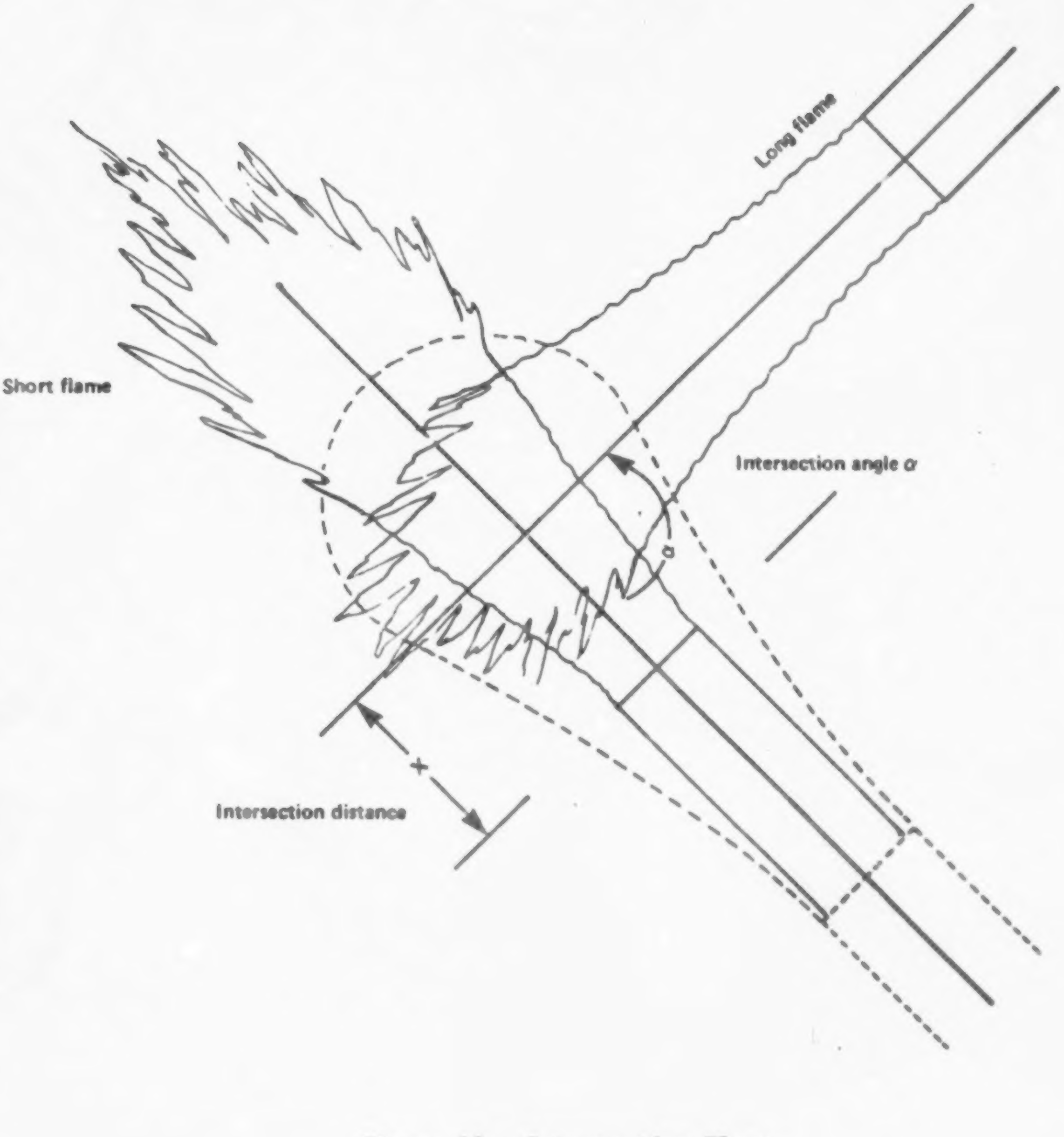
Long flame
Short flame
Intersection angle α
α
x
Intersection distance

Figure 10. Intersecting Flame

TABLE IA. COAL ANALYSIS

Proximate (% Wt) / Coal	Montana	Virginia	W. Kentucky
Moisture	21.23	0.31	5.0
Volatiles	35.16	31.9	36.55
Fixed Carbon	34.27	51.4	50.98
Ash	9.34	16.5	7.47
Rank	Sub-bit. C.	High-Vol. A	High-Vol. B
Ultimate (% Wt)			
Carbon	53.26	71.11	69.79
Hydrogen	3.35	4.46	4.79
Nitrogen	0.87	1.68	1.34
Oxygen	11.16	4.24	8.65
Sulfur	0.78	2.02	2.95
Ash	9.34	16.5	7.47
Heat of Combustion Btu/lb	8,972	14,079	12,349

TABLE IB. OIL AND COM ANALYSIS

Mixture 30% (Wt) Coal / Analysis	W. Kentucky/ Amerada	Montana/ Amerada	Montana/ Chevron	Virginia/ Chevron	Amerada Hess #6	Chevron #6
Carbon	80.23	75.27	75.88	81.23	84.71	85.57
Hydrogen	9.00	8.57	8.37	8.70	10.75	10.52
Nitrogen	0.63	0.49	0.83	1.07	0.36	0.81
Oxygen	3.92	4.67	4.77	2.73	1.93	2.08
Sulfur	2.44	1.79	0.89	1.26	2.22	0.93
Ash	2.26	2.82	2.87	4.95	0.93	
Moisture	1.52	6.39	6.37	0.09		
Heat of Combustion Btu/lb	17,600	16,600	15,500	17,000	19,867	18,292
API Gravity					15.3	12.3
Flashpoint COC°F					204.0	182.0
Viscosity, SSU at 100°F					2,500	4,900.0

TABLE II. RDF FUEL ANALYSES

Ultimate Analysis*	Fuel Type				
	Pittsburg No. 8 Coal	Richmond Refuse	Ames Refuse	Americology Refuse	San Diego Refuse
Carbon %	75.23	42.60	40.49	40.29	38.01
Hydrogen %	5.15	6.26	6.01	5.88	5.64
Oxygen %	8.12	37.90	30.04	25.20	17.40
Nitrogen %	1.49	0.83	0.73	0.91	0.69
Sulfur %	2.51	0.16	0.35	0.17	0.21
Ash %	7.50	12.25	22.38	27.55	38.05
Moisture % (as received)	0.93	23.8	15.2	24.4	26.3
Chlorine %	0.14	.46	.43	.72	.79
Heating Value Btu/lb	13,545	7696	7831	7164	7146

*Dry Basis

TABLE III. EFFECT OF RDF TYPE ON PARTICULATE SIZE DISTRIBUTION

	Filter	>10μ	>3μ	>1μ
Fuel	Qty (gr/ft^3) %	Qty (gr/ft^3) %	Qty (gr/ft^3) %	Qty (gr/ft^3) %
20% Ames + Nat Gas	0.039 (69)	0.011 (19)	0.003 (6)	0.004 (6)
20% Richmond + Nat Gas	0.032 (91)	0.0004 (1.)	0.0004 (1)	0.0024 (7)
20% Americology + Nat Gas	0.041 (86)	0.002 (5)	0.002 (5)	0.002 (5)
20% San Diego + Nat Gas	0.062 (80)	0.007 (9)	0.002 (3)	0.006 (8)

TABLE IV. EFFECT OF COAL & RDF CONCENTRATION ON PARTICULATE SIZE DISTRIBUTION

Fuel	Filter	>10μ	>3μ	>1μ
	Qty (gr/ft^3) %	Qty (gr/ft^3) %	Qty (gr/ft^3) %	Qty (gr/ft^3) %
20% Richmond RDF + Coal	.026 (9.1)	.134 (47.3)	.107 (38.0)	.016 (5.5)
10% Richmond RDF + Coal	.044 (7.6)	.269 (46.1)	.226 (38.8)	.044 (7.6)
Coal Only	.021 (2.1)	.539 (56.3)	.344 (35.9)	.055 (5.7)

TABLE V. TRACE METAL CONCENTRATION FOR COAL VS 10% RDF + COAL VS 10% RDF + GAS (μg/Btu)

ELEMENT	Coal Only Test #40[a]	10% RDF + Coal Test #38[a]	10% RDF + Gas Test #11b[a]
Cu	1.9581	<0.3319	0.3402
Zn	0.5294	0.8227	0.4468
Mn	0.1526	<0.2693	0.0209
Pb	17.5319	0.3091	1.4996
Cd	0.0091	0.0048	0.0062
Be	<0.0176	0.0013	<0.0034
Ti	<1.7540	<0.0587	<0.0277
Sb	<0.0020	<0.0090	0.0333
Sn	0.1300	<0.0913	<3.5033
Hg	<0.0015	<0.0173	<0.0009
As	<0.0881	<0.0323	<0.0184

[a] 20% excess air

TABLE VI. ORGANICS FOUND

Test Condition	Organic	Amount (ug/10^6 Btu)
Gas Cofire 10% RDF 20% EA Ames Fuel	Fluoranthene Pyrene	10 332
Gas Cofire 10% RDF 20% EA Richmond Fuel	Phenanthrene Fluoroanthene Pyrene Diphenyl Ether Biphenyl Phenylether	64 160 576 3395 1697
Gas Cofire 10% RDF 20% EA Americology Fuel	Phenanthrene Pyrene	5[illegible] 101
Coal Cofire 10% RDF 20% EA	Phenanthrene	98

TABLE VII. PHASE IV -- LOW NO_X TANGENTIALLY FIRED SYSTEM

TASK A

Tangentially fired system definition and evaluation

-- chemical/physical processes defined

-- early mixing evaluated

-- flame processing of NO in intermediate and far zone evaluated

TASK B

Optimization of tangentially fired near and intermediate zone NO

-- early mixing, cooling, and entrainment of flue gas optimized

-- intermediate zone mixing, cooling, and entrainment of flue gas optimized

TASK C

Optimization of low NO_X tangentially fired systems for several coals

-- optimal burners in firebox with optimal fuel/air feeding of the fireball

POLLUTANT FORMATION DURING FIXED-BED AND SUSPENSION COAL COMBUSTION

By:

D. W. Pershing
B. D. Beckstrom
P. L. Case
G. P. Starley

Department of Chemical Engineering
University of Utah
Salt Lake City, Utah 84112

ABSTRACT

This paper summarizes the overall scope and the progress made during the first five months of a grant to study the formation of pollutant species, particularly nitrogen and sulfur oxides, during the fixed-bed and suspension combustion of coal. The work will consider conditions typical of both pulverized and stoker-fired coal systems with the major emphasis on spreader/stoker fired boilers and furnaces. Specifically the program will consider: 1) the evolution and oxidation of fuel nitrogen and sulfur; 2) the retention of sulfur oxides by the ash and/or solid chemical sorbents in suspension- and fixed-bed burning; and, 3) the effectiveness of distributed air addition for nitrogen oxide control. In addition, the study will attempt to quantify the combustion process in a stoker environment and consider possible detrimental effects of control technology on boiler operation.

The approach is primarily experimental, utilizing a controlled mixing history furnace and fixed-bed reactor to investigate suspension and fixed-bed combustion, respectively. In addition, a model spreader/stoker system will be fabricated, characterized, and used for evaluating advanced combustion control concepts. The suspension furnace has now been designed and most of the refractory casting is complete. The flow-control system for this furnace has been specified and essentially all of the required instrumentation has been procured. Design of the fixed-bed furnace has just been initiated.

ACKNOWLEDGMENTS

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PURPOSE AND SCOPE

This paper describes the progress of an investigation to study the formation of air pollutant species, particularly NO, NO_2, SO_2, and SO_3, during the combustion of coal particles with a view toward providing technology for the design of high-efficiency, low-emission boilers and furnaces. The work will consider conditions typical of both pulverized-coal and stoker-fired systems, but the emphasis will be on the latter because they represent a major source which has been largely overlooked previously.

At present stoker-fired boilers are significant in terms of both coal consumption and environmental impact. In 1974 almost 20 percent of the coal consumed in the United States was burned in stoker systems. Stoker-fired, water-tube boilers are the single largest source of particulate emissions and the fourth largest source of SO_x emissions, because neither is in general controlled. They account for 13 percent of the NO_x emissions from all coal systems and their environmental impact may be even more significant than indicated by the mass emissions, because stoker systems are often located in congested metropolitan areas. Further, the energy and environmental importance of stoker firing seems certain to grow with the increase in industrial coal utilization that is projected. It is important, therefore, that further knowledge be obtained on the formation and control of nitrogen and sulfur oxides under conditions typical of stoker firing.

In particular, this program will consider the following major research areas:

1. The evolution and oxidation of fuel nitrogen and sulfur;
2. The retention of sulfur oxides by ash and/or solid-chemical sorbents in both suspension- and fixed-bed burning;
3. The effectiveness of distributed air addition for NO_x control in both pulverized- and stoker-fired coal systems.

In addition, the study will attempt to quantify the combustion process in a stoker environment and consider possible detrimental effects of control technology on boiler operation.

The approach is primarily experimental, utilizing a controlled mixing history furnace and a fixed-bed reactor to investigate suspension and thick-bed combustion, respectively. In addition, a model spreader-stoker system will ultimately be fabricated, characterized, and used for evaluating advanced combustion control concepts. The next section of the paper describes the details of the approach. The third and fourth sections then discuss the progress made during the first five months of the program.

APPROACH

OVERVIEW

This study is scheduled for three years and is divided into five separate tasks:

Task 1: Preparation of a detailed program plan.
Task 2: An experimental investigation of suspension burning of bituminous coal.
Task 3: An experimental investigation of fixed-bed burning of bituminous coal.
Task 4: An experimental and analytical optimization of combustion modification technology using a model stoker system.
Task 5: Experimental studies to extend the control-technology results to other fuels.

Each task is discussed in detail in the following paragraphs. Tasks 1, 2, and 3 have been initiated. Task 4 will start in the second year of the program and Task 5 will begin in the third year.

EXPERIMENTAL PLAN PREPARATION

Work is currently underway on a detailed program plan for the first eighteen months of the study. It will include a description of the initial experiments to be conducted in each task and detailed designs for the fixed-bed and suspension experimental furnaces. To ensure the practicality of the proposed experimentation, conversations will be held with stoker manufacturers and users to define in detail the problems associated with industrial stoker usage, the current trends, and future utilization of stoker technology. This will include site visits to at least one fabricator, one industrial user, and other researchers in the field.

SUSPENSION BURNING

The purpose of the second task is to investigate the formation of pollutant emissions during the suspension-burning phase of the combustion process. These studies are intended to be relevant to both pulverized-coal combustion and the suspension-burning phase of a spreader/stoker system. Initial studies will focus on the relationship between the combustion parameters and the evolution and subsequent oxidation of nitrogen and sulfur species. The role of fuel-bound nitrogen in the formation of NO_x will be established, both for small particles that are essentially completely burned in the suspension phase and for large particles that only undergo partial oxidation. The possibility of gas-phase sulfur capture will also be explored in this task.

Both the furnace and the flow-control system for the suspension-phase studies have been designed as described in the next section of this paper. Furnace fabrication is now more than 50 percent complete and essentially all of the components for the flow-control system have been procured.

FIXED-BED COMBUSTION

The purpose of the third task is to utilize a simple, relatively inexpensive experimental test facility to study the combustion of coal in a fixed-bed environment. The experimental system will be designed to provide a Lagrangian simulation of the time/temperature/environmental history seen by a small section of the stoker bed as it passes through an actual furnace. Both thick- and thin-bed systems will be considered. The use of a simple, fixed-bed coal furnace will allow evaluation of a large number of different conditions, fuels, and additive materials without the complications associated with moving stoker grates.

The design of the experimental system has not yet been resolved; however, it is likely that the fixed-bed furnace will be a refractory chamber with a removable bed section and auxiliary gas heating capability. Thermocouples and sampling probes will be positioned both within the bed and above the bed. Provisions will be made for independent control of both underfire and overfire air. Present plans are to design the bed for firing rates up to 400,000 Btu/ft^2/hr at a coal-feed rate of 20 lbs/hr.

The first set of experimental studies will focus on the relation between fixed-bed combustion parameters and overall pollutant emissions. The parameters of interest include:

- . Bed composition
- . Bed thickness
- . Bed and gas-phase temperature
- . Free-stream composition (stoichiometry)
- . Particle size
- . Bed-heating rate and amount
- . Bed-residence time
- . Amount and location of overfire air

Later testing will focus on the evolution and subsequent oxidation of fuel-nitrogen and sulfur species both within and above the bed. Measurements of nitrogen and sulfur intermediates (e.g. NH_3, HCN, H_2S, etc.) will be attempted. Solid samples will be removed from the bed after various residence times and analyzed for ultimate composition. Other studies will investigate the sulfur-retention capabilities of the coal ash itself and the potential of solid sorbent materials. Of particular interest will be the distribution of the sorbent materials throughout the bed.

MODEL STOKER STUDIES

The purpose of the fourth task is to apply the pollutant reduction concepts developed in Tasks II and III to an actual stoker environment. An experimental furnace will be fabricated to directly simulate both spreaker/stoker and fixed-bed systems. Initial experiments will be conducted to define the interaction between the suspension burning and the fixed-bed combustion since each of these will have been considered separately in the previous tasks. Later testing will be directed toward defining and optimizing new combustion control technology.

ALTERNATE FUELS

The purpose of the final four-month task is to study the impact of coal composition on combustion control technology. It is anticipated that the fuels to be studied here will include at least one desulfurized coal, a lignite, and perhaps a markedly different alternate fuel such as wood chips.

SUSPENSION BURNING

The suspension furnace was designed to meet the following criteria:

1. Capable of simulating the environment seen by a particle in the suspension burning phase of spreader/stoker combustion or in the burner zone of a PF furnace.
2. Independent wall-temperature control with high-temperature capability.
3. Adequate probing and visual access.
4. Variable residence time.
5. Well defined fluid dynamics.

The final furnace design utilizes three types of interchangeable furnace sections. In each case the innercombustion chamber is 6 inches in diameter and the outer steel shell is 28-inches square. A cylindrical innerchamber was chosen (in preference to a square one) because it is more amenable to analytical modelling at some later date. A square outside surface was selected because it reduced the cost of fabrication and provided a more suitable base for mounting probes, thermocouples, etc.

The walls of the main furnace sections consist of an outer steel shell, 5 inches of 1900°F insulating block, 4 inches of 2500°F insulating refractory, and 2 inches of 3400°F high-temperature castable refractory. Each of the mid-sections contain 5 2-inch diameter ports for second-stage air injection and/or insertion of species and temperature probes.

As presently conceived, the furnace can be operated in two modes: The self-sustaining flame mode and the tubular-reactor, control-mixing history mode. Figure 1 illustrates the first mode in which the pulverized coal and at least part of the combustion air (or artificial atmosphere) enter the combustion chamber at the top via a premixed burner. Current plans are to use the premixed burner developed by Howard and Essenhigh (1). A modification of this burner system has proved suitable for studying NO_x formation in premixed, one-dimensional flows (2). This mode of operation will be used for characterizing the nitrogen and sulfur evolution for particle sizes and size distributions smaller than 50 percent through 100 mesh (i.e., pulverized coal and the fines in stoker-coal system). In this mode, the flue gases will exit at the bottom of the furnace through the horizontal section.

In order to simulate the temperature and environment of the suspension-phase burning in a spreader/stoker system, the second mode of operation will be utilized (Fig. 2). In this case, a high-intensity gas burner will be attached to the horizontal extension at the furnace bottom. The large, stoker-sized coal particles will be fed from the top of the furnace and allowed to fall downward into the stream of hot combustion products flowing vertically upward. In this case, the premixed coal burner will be replaced with a large, multihole coal injector and the majority of the combustion air will be supplied from the bottom with the gas flame. In an actual spreader/stoker system, the suspension phase combustion occurs with reduced oxygen concentrations (less than 10 percent) and with both nitrogen and sulfur species already present from the fixed-bed combustion. To simulate this, SO_2 and/or ammonia will be added to the gas flame to produce the concentrations of SO_2, SO_3, NO, and NO_2 that would normally be present in the combustion gases leaving the stoker bed. Both acetylene and methane will be used as fuels for the gas burner to investigate potential XN/hydrocarbon interactions. In this mode, the main flue gases will exit at the top of the furnace through the horizontal section as shown (Fig. 2).

As shown in Fig. 3, the side walls have provision for auxiliary heating (or cooling) by firing natural gas or passing cooling air through outer channels. These channels are 2 inches in width and cover 50 percent of the circumference. This will allow partial independent control of the radient heat transfer to the particles and more complete control of wall temperature. The auxiliary firing sections are completely interchangeable so any portion of the furnace can be heated (or cooled).

The flow-control system for the suspension furnace has been designed and the required components procured. The flow system was selected to provide precise metering of the streams entering the main combustion chamber and adequate control of the other auxiliary gas and air streams. Flow metering and control of the following subsystems are included:

1. Main-chamber air.
2. Side-burner air.
3. Auxiliary-burner air.
4. Artificial oxidants
5. Side-burner gas.
6. Auxiliary-burner gas.

The combustion air is supplied by a 100 SCFM, 100 psi rotary vane compressor. Primary, secondary, and tertiary air are metered with 600 mm high acuracy Brooks rotameters. The second-stage air is metered with a large, 10-inch Dwyer rotameter. All other air and gas flows are metered with 10-inch Dwyer rotameters. The flow system also includes an artificial oxidant supply, so that the combustion air can be completely replaced with an atmosphere composed of argon, carbon dioxide, and oxygen in varying proportions. In each case, the pure gases are supplied from high-pressure cylinders and metered with rotameters.

ANALYTICAL MEASUREMENTS

The furnace exhaust gases will be continuously monitored for NO, NO_2, CO, CO_2, and O_2. Using the instrumentation listed below:

Gases	Instrument
NO, NO_2	Thermoelectron, Model 10AR, chemiluminescent analyzer
CO, CO_2	Anarad, Model AR-600 NDIR
O_2	Beckman, Model 755, paramagnetic oxygen analyzer

The other stable, gas-phase pollutants and intermediate species of interest will be measured on a batch bases. These include hydrogen sulfide (H_2S), sulfur dioxide, and trioxide (SO_2, SO_3), carbonyl sulfide (COS), carbon disulfide (CS_2), ammonia (NH_3), and hydrogen cyanide (HCN). SO_3 will be measured using the standard ASTM condensation method. Measurement of NH_3 will be attempted using the Axworthy chemiluminescent technique. The other species (SO_2, H_2S, COS, CS_2, and HCN) will be analyzed with a Hewlett-Packard, Model 5830A, dual column, temperature programmable gas chromatograph. The sulfur compounds will be sensed with a flame photometric detector. The nitrogen containing species (e.g., HCN) will be measured with the rubidium-bead nitrogen/phosphorus flame detector. Current plans are to use an acetone washed 1/8-inch teflon tube, 4 feet long, packed with acetone washed Porapak QS for separation of the sulfur compounds (after deSouza (3)).

REFERENCES

1. Howard, J. B. and R. H. Essenhigh. Pyrolysis of Coal Particles in Pulverized Fuel Flames. Ind. Eng. Chem., Process Design and Development, 6 (1), 1967.

2. Wendt, J. O. L., J. W. Lee, and D. W. Pershing. Pollutant Control Through Staged Combustion of Pulverized Coal. FE-1817-4, U. S. Department of Energy, Washington, D.C., 1978. 158pp.

3. de Souza, T. L. C., D. C. Lane, and S. P. Bhatia. Analysis of Sulfur-Containing Gases by Gas-Solid Chromatography on a Specially Treated Porapak QS Column Packing. Analytical Chemistry, 47 (3), 1975.

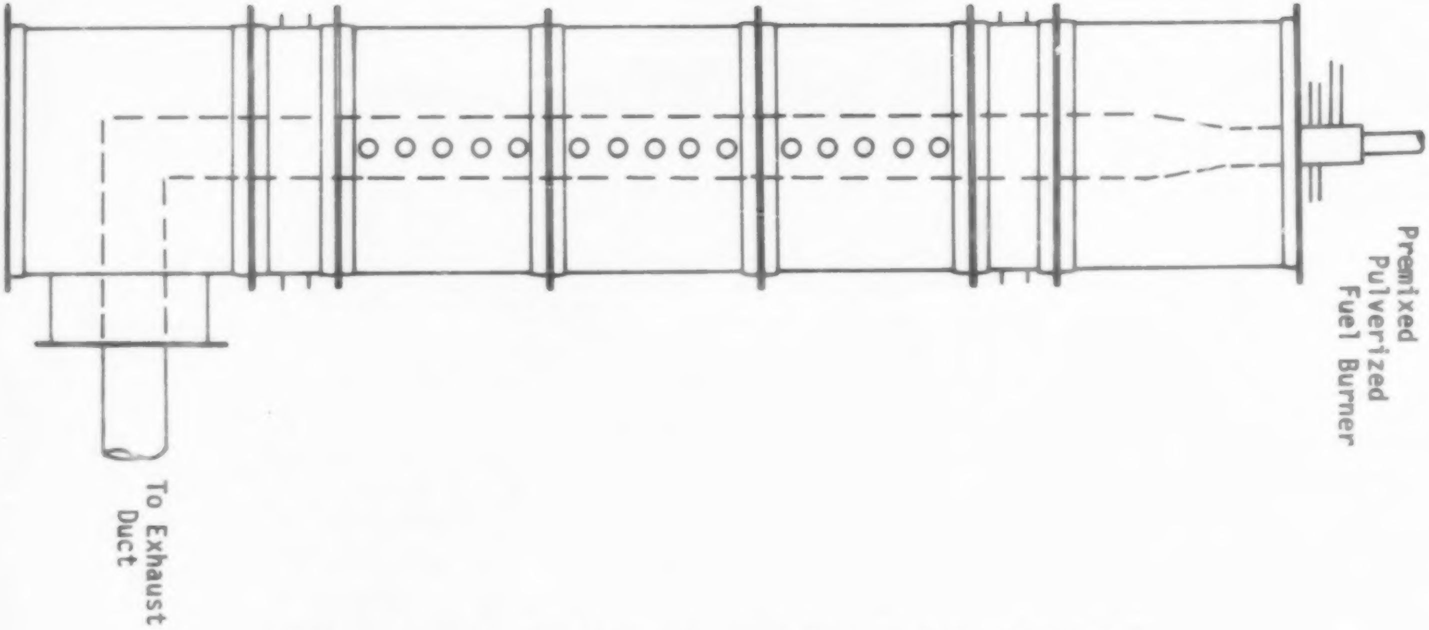
Premixed
Pulverized
Fuel Burner
To Exhaust
Duct

Figure 1. Suspension Furnace - Self-sustaining Flame Mode

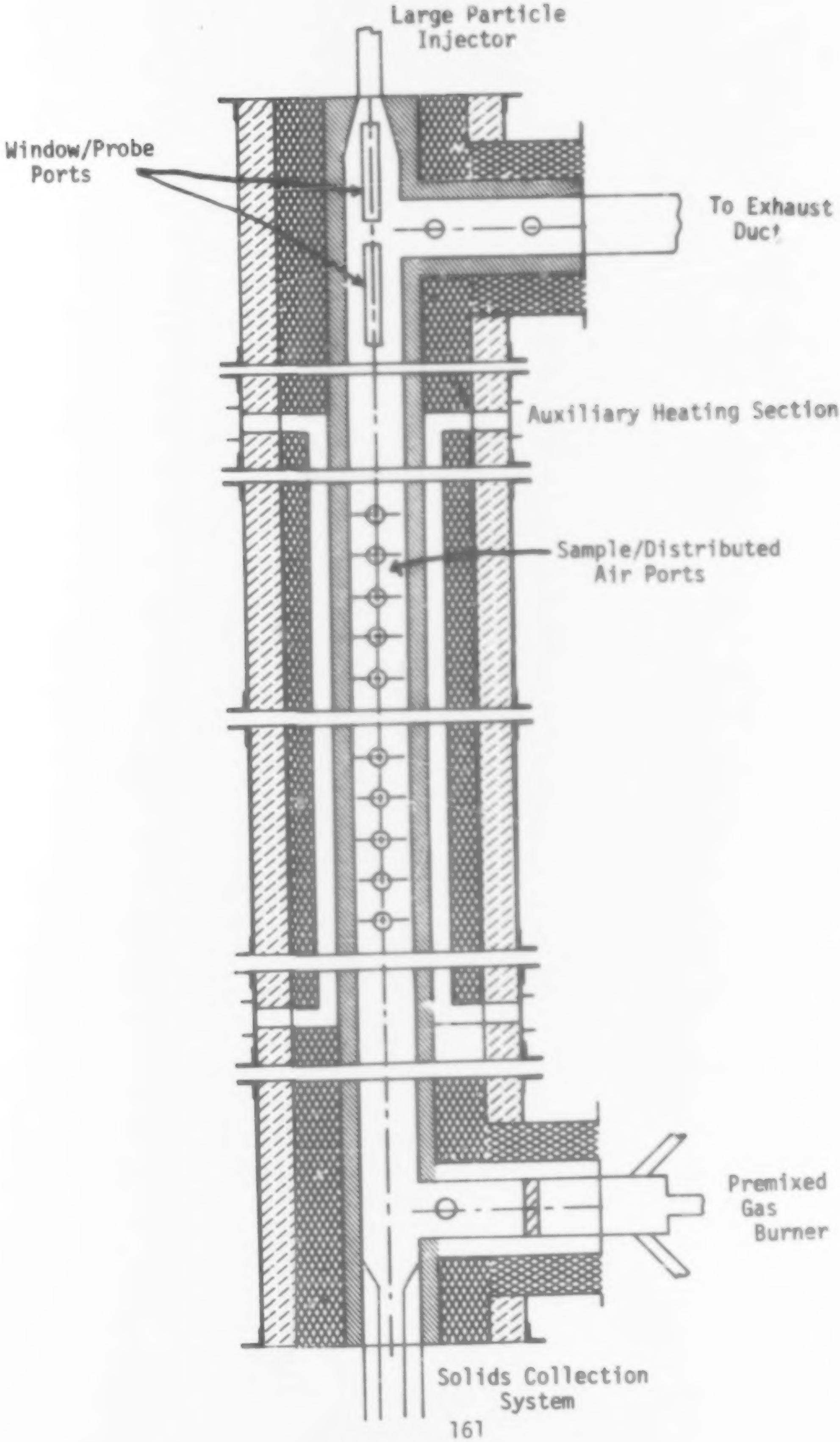
Large Particle Injector
Window/Probe Ports
To Exhaust Duct
Auxiliary Heating Section
Sample/Distributed Air Ports
Premixed Gas Burner
Solids Collection System

Figure 2. Suspension Furnace - Tubular Reactor Mode

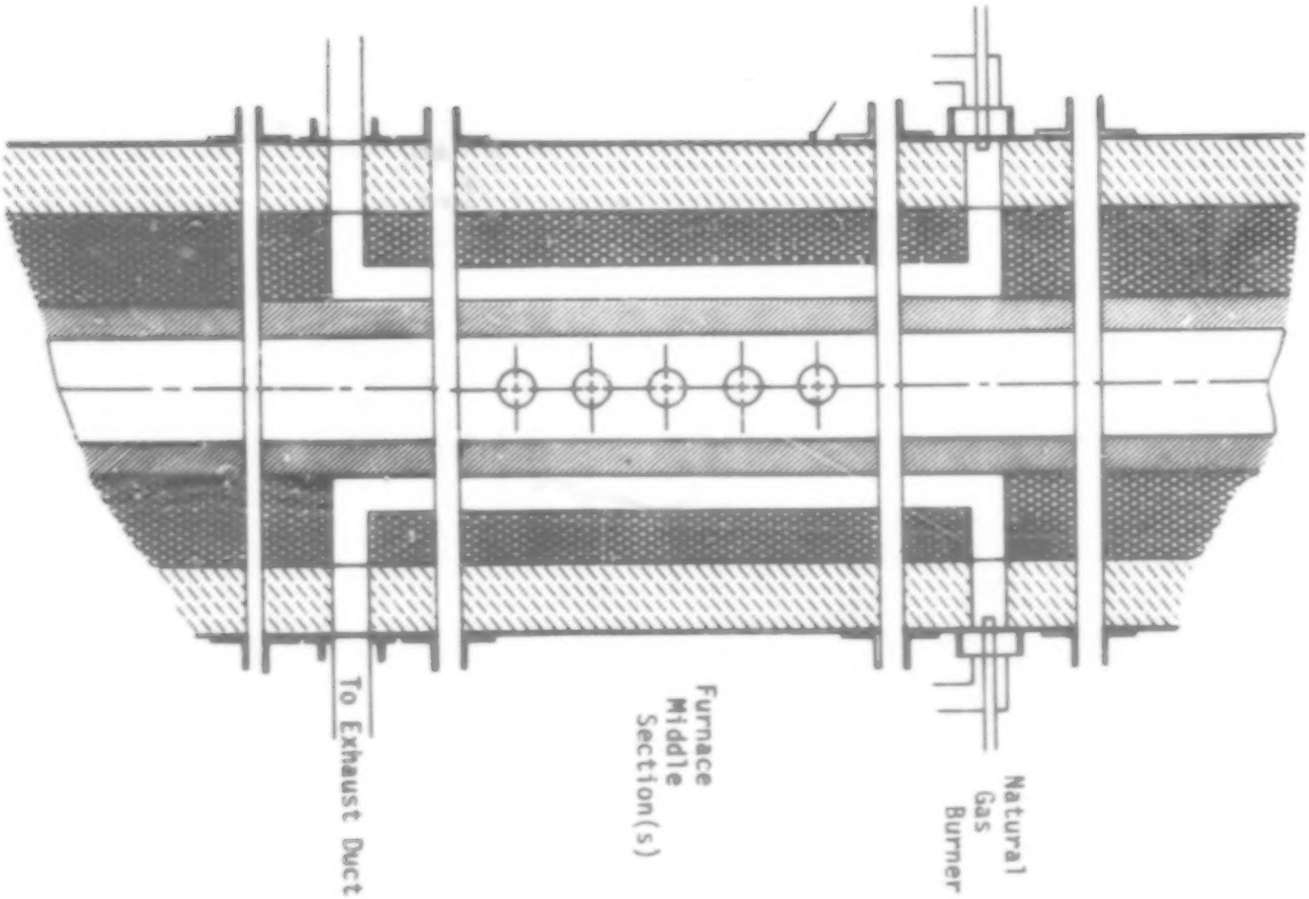
To Exhaust Duct
Furnace Middle Section(s)
Natural Gas Burner

Figure 3. Detail of Auxiliary Heating (Cooling) System

ADVANCED COMBUSTION CONCEPTS
FOR
LOW BTU GAS COMBUSTION

By:

B. A. Folsom
C. W. Courtney
T. L. Corley
W. D. Clark
Energy and Environmental Research Corporation
Santa Ana, California 92705

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ABSTRACT

The low Btu gas combined cycle power plant is an alternative to the direct coal-fired steam cycle with the potential for low sulfur emissions and high overall efficiency. However, low Btu gas contains ammonia which could lead to high nitrogen oxide emissions.

This paper discusses the development of low NO_x combustor concepts for this application. The thermodynamic performance of several alternative low Btu gas-fired combined cycles is investigated and the combustor operating conditions necessary to optimize thermodynamics performance are identified.

A kinetic mechanism describing fuel nitrogen conversion to NO is used to analyze idealized combustors with these operating conditions and several potential low NO_x combustor concepts are investigated.

Synthetic low Btu gases with varying compositions were fired in three atmospheric pressure flame reactors: diffusion flame reactor, premixed flat flame reactor, and premixed catalytic reactor. NO_x emissions were found to be sensitive to the concentrations of ammonia and hydrocarbon gases in the low Btu gas. Lowest NO_x emisssions were produced by the diffusion flame reactor operating fuel-lean and the catalytic reactor operating fuel-rich.

ACKNOWLEDGEMENTS

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SECTION 1

INTRODUCTION

This paper discusses the development of low nitric oxide (NO) emission combustors for low Btu gas (LBG)-fired combined cycle power systems. The rising demand for electrical power coupled with the limited availability of petroleum makes the construction of many alternate fuel-based power plants by 1985-1990 very desirable. Since these plants will commence operation in the future when environmental restrictions will probably be much more restrictive than at present, the environmental design goals should be to minimize emissions rather than to meet current New Source Performance Standards.

Several advanced coal-based power cycles are currently being developed for this application (1,2,3,4). The integrated gasifier LBG-fired combined gas turbine-steam turbine cycle is one of these alternatives. The primary advantage of this cycle is the potential for low emission of sulfur products without the economic and efficiency penalties associated with stack gas sulfur removal (5,6). Since the coal gasification process operates fuel-rich, the sulfur in the coal is converted mainly to hydrogen sulfide (H_2S) in the low Btu offgas which can be removed (potentially) more easily than sulfur dioxide (SO_2). Energy losses associated with the gasification and cleanup process can amount to as much as 30 percent of the coal's heating value. However, if the clean LBG is fired in a gas turbine combustor as part of a combined cycle power plant the gains in overall power plant performance, when compared to conventional steam cycles, may more than offset the losses in the gasification and cleanup processes.

The minimization of NO emissions from LBG-fired combined cycles is an important and at present unsolved problem. In the gasification process, some of the nitrogen in the coal is converted into ammonia (NH_3) in the LBG. Under typical gas turbine combustor operating conditions a large fraction of the NH_3 may be converted to NO resulting in significant emission.

The concentration of NH_3 in the LBG depends upon gasifier design and operating parameters and may be as high as 0.38 percent (6). The gas cleanup system, which functions primarily to remove sulfur products and particulates from the LBG, may remove a portion of NH_3, but the remainder will enter the gas turbine combustor and may be oxidized to nitrogen oxides (NO_x). A concentration of 0.38 percent NH_3 in the LBG would produce approximately 1370 ng/J (3.2 lb $NO_2/10^6$ Btu) if all NH_3 is converted to NO_2. At present there are no New Source Performance Standards (NSPS) for LBG fired combined cycle power systems. However, it is reasonable to expect that when NSPS are promulgated they will be at least as stringent as current NSPS for other power systems such as gas turbines or gas fired steam generators. The current NSPS for gaseous fossil fuel-fired steam generators with greater than 73.3 MW (250×10^6 Btu/hr) heat input is 86 ng/J (0.2 lb $NO_2/10^6$ Btu) (7). For a combined cycle firing an LBG with 0.38 percent NH_3 to meet this emission level, the overall conversion of NH_3 to NO would have to be less than 6.3 percent. It is well-known that the conversion of fuel nitrogen compounds (such as NH_3) to NO_x is sensitive to combustor design and operating parameters. A recent analytical study of combustion modification techniques applied to LBG-fired combined cycle combustors has demonstrated the potential for significant reductions in NO_x emissions (8).

The development of low NO emission combustor concepts for LBG-fired combined cycle systems is the objective of a current Environmental Protection Agency program (Contract No. 68-02-2196, G. Blair Martin, Project Officer). This paper presents some preliminary analytical and experimental results from this program. The following section discusses combustor design requirements based on maximizing the thermodynamic performance of LBG-fired combined cycles. The subsequent section outlines a kinetic mechanism for NO formation from NH_3 and presents several low NO_x combustor concepts based upon kinetic analysis. The next section presents the results of combustion experiments burning synthetic low Btu gases with varying compositions in several types of combustors. Discussion and conclusions follow.

SECTION 2

DEFINITION OF COMBUSTOR REQUIREMENTS

Figure 1 is a simplified schematic diagram of an LBG-fired gas turbine-steam turbine combined cycle power plant with integrated gasifier. Only the major heat, work and mass flow paths have been shown for clarity. The system consists of a gas turbine topping cycle with exhaust heat transferred to a steam turbine bottoming cycle through a waste heat recovery boiler. Low Btu gas is produced in a gasifier supplied with coal, compressed air from the gas turbine air compressor, and steam from the bottoming cycle. This "integration" with other cycle components significantly reduces the energy losses attributable to the gasification process.

"Raw" LBG exits the gasifier at temperatures as high as 1370 K depending upon gasifier design and operation containing three pollutant precursors:

- Sulfur compounds which can be oxidized to SO_x in the combustor,
- Particulates including carbon, tars and ash which may damage turbine blades and may be emitted to the atmosphere, and
- Ammonia which may be oxidized to NO_x in the combustion process.

Raw LBG is processed through a gas cleanup system to reduce the concentrations of these materials prior to combustion. Several gas cleanup systems have been developed or are under development for this application (9). Hot gas cleanup systems process the LBG without significantly reducing its temperature and remove a majority of sulfur products and particulates. Cold gas cleanup systems require cooling the LBG to near ambient temperature (400 K) and remove a majority of the sulfur products and particulates. They may also remove a substantial portion of the ammonia. The sensible heat removed from the LBG may be used for a variety of purposes, but it effectively bypasses the gas turbine topping cycle and contributes to reduced efficiency. The thermodynamic trade-offs in hot and cold gas cleanup processes have recently been investigated (8,10). Depending upon gasifier design and operating parameters, the sensible heat in LBG offgas can amount to as much as 20 percent of the total heat release and the losses due to intercooling the LBG with a cold gas cleanup system can be substantial.

From a combustor design point of view, the choice of a hot gas cleanup system as opposed to a cold system could well have two important effects:

- Higher adiabatic flame temperature
- Higher NH_3 concentration

The sensible heat in the LBG contributes directly to the adiabatic flame temperature. For typical LBG compositions, cooling the gas by 400 K will decrease the adiabatic flame temperature at stoichiometric conditions by about 200 K, thus reducing the potential for thermal NO_x formation. If a low temperature cleanup system is employed, a substantial portion of the NH_3 may be removed. Residual NH_3 concentrations of 100 to 400 ppm have been predicted for full-scale systems (3,4). These concentrations correspond to approximately 34 to 145 ng/J (0.08 to 0.34 lb $NO_2/10^6$ Btu) for full conversion. While the lower prediction meets current NSPS (neglecting the contribution from thermal NO_x), further NO_x control may be necessary to meet future standards.

The term low Btu gas does not refer to a specific gas composition, but rather to a family of fuels produced by reforming coal with air and steam. The heating value of LBG may range from 16,000 to 41,000 J/m^3 (80 to 200 Btu/ft^3) and the primary combustible specie are CO and H_2. The ratio of CO to H_2 concentrations ranges from 0.5 to 2. Hydrocarbon fuel gases (normally CH_4) may also be present in quantities up to 10 percent, and nitrogen is the primary diluent comprising 35 to 55 percent of the fuel gas. Other diluents include CO_2 and H_2O. Trace amounts of H_2S, COS and NH_3 may also be present, since these specie are not entirely removed by the gas cleanup system. The relationship between LBG composition and combustor performance is currently under investigation as part of this program and Section 4 discusses the performance of combustor firing LBGs with a wide range of compositions.

Combustor operating conditions are dictated by thermodynamic and materials considerations. High turbine inlet temperature (TIT) is desirable for improved thermodynamic performance. Current materials and blade cooling technology limit TIT for stationary gas turbines to 1273 K to 1473 K. The combustor pressure producing an optimum balance between cycle efficiency and specific work output is usually about 12 atmospheres. The corresponding compressed air temperature for high efficiency compressors is about 638 K. Improvements in high temperature materials and turbine blade cooling are expected to increase allowable TIT in the future. One proposed LBG-fired combined cycle was designed around a 1644 K TIT (4).

If the exhaust heat from an optimized gas turbine cycle precisely matched the heat requirements of an optimized steam turbine cycle there would be no need for cycle variations. However, the gas turbine exhaust temperature is usually too low for an optimized steam turbine cycle. The overall efficiency of the combined cycle can be improved by modifying the cycle arrangement to reduce the mismatch between the energy content of the gas turbine exhaust and energy requirements of the steam turbine cycle. This can be accomplished by incorporating any of the cycle modifications listed below.

- Direct fired turbine exhaust heater
- High excess air supercharged boiler gas turbine combustor
- Reheat gas turbine cycle

The thermodynamic performance of LBG-fired combined cycles incorporating these cycle modifications was analyzed as part of this program and the analytical details are discussed in references 8, 10, 11, 12 and 13. The results are summarized in Table 1 which lists the overall efficiency and combustor operating conditions for these cycles with two TITs: 1366 K typical of state-of-the-art stationary gas turbines and 1700 K which may be achievable in the future utilizing advanced turbine blade cooling techniques. These results were calculated subject to the component efficiencies and other assumptions listed in Reference 10. Since these assumptions may not necessarily be fulfilled in future generation combined cycle systems, the efficiencies and operating conditions listed should be considered as approximate.

The combustors listed in Table 1 can be grouped into two general types: primary combustor where the oxidant is nonvitiated compressed air, and secondary combustors where the oxidant is the partially vitiated combustion products from the primary combustor. The primary combustors will operate at several atmospheres pressure with warm air (from the heat of compression) and will generate a hot gas stream for the turbine. They will operate either adiabatically or with only a small amount of heat (less than 20 percent) transferred to the bottoming cycle. The overall stoichiometry will be very fuel-lean, greater than 250 percent theoretical air. The NO_x control goals for primary combustors are to minimize conversion of NH_3 in the LBG to NO_x (fuel NO_x) and minimize formation of NO_x from N_2 (thermal NO_x).

The secondary combustors will operate at pressures less than the primary combustors and may produce either a hot gas stream for a low pressure turbine or a warm gas stream for a waste heat recovery boiler. The overall stoichiometry of these combustors will be fuel-lean but richer than the primary combustors. The amount of heat released in the secondary combustors will be small compared to the primary combustors. The NO_x control goals for secondary combustors are the same as for primary combustors except that additional NO_x control might be achieved by reducing some of the NO_x formed in the primary combustor to N_2.

SECTION 3

NITRIC OXIDE FORMATION IN LBG-FIRED COMBUSTORS

Tyson et al. (14) have assembled a kinetic reaction set based upon the work of many investigators which describes the formation of NO and N_2 in combustible mixtures of CO, H_2 and CH_4. Those reactions involving nitrogenous species are presented in Table 2. Ammonia breakdown occurs via hydrogen abstraction allowing nitric oxide formation by the oxidation of any of the nitrogenous fragments. Under fuel-lean conditions, Reaction 4 predominates and the major portion of the NH_3 is converted to NO. Under fuel-rich conditions NO might still be formed via Reaction 4 if all the oxygen has not been consumed, or by Reaction 6. Hydrogen cyanide has been observed by several investigators, and for high temperature flames Morley (15) has shown that regardless of their nature, nitrogen compounds are quantatively converted to HCN in the reaction zone of premixed rich (less than 80% theoretical air) hydrocarbon flames. Hydrogen cyanide formation from NO could be possible by reactions such as 7 and 8. Hydrogen cyanide can also be produced from molecular nitrogen via reaction with hydrocarbon radicals (16). The subsequent oxidation of HCN allows the interchange of XN specie since NH is one of the specie formed as HCN is oxidized via the intermediary NCO. Once NH is present then the reverse of Reactions 1, 2 and 3 allows the formation of ammonia. Nitrogen formation can occur via the reverse of Reaction 5, or by reaction with NO and other nitrogenous species. Although Reaction 13 is included in Table 3, there is some question as to whether a reaction of this type can take place. The reactions shown in Table 3 illustrate how ammonia in LBG could be converted to either N_2, NO, HCN or back to NH_3 in rich combustion products. Since N_2 is thermodynamically favored at certain reactant stoichiometries and temperatures, the objective of the combustor designer is to provide the most favorable temperature and stoichiometry histories to maximize N_2 production and thus minimize total bound nitrogen species (ΣXN).

Decoupling the practical considerations of the fuel/air contacting process, it would appear that several combustor configurations might minimize NO_x emissions from LBG containing NH_3. Four such concepts were analyzed by applying the kinetic mechanism described above to idealized combustor models consisting of various combinations of well-stirred and plug flow modules.

The simplest case considered was the rich/lean series staged combustor shown in Figure 2. The ignition reactor provides the feedback of heat and radical species for flame stabilization and the plug flow reactor, which operates at an optimum stoichiometry, allows sufficient time for the reactions listed in Table 2 to proceed towards equilibrium. Secondary air is added uniformly over a short time period to burn out the remaining combustibles and to dilute the combustion products to the desired TIT.

This combustor configuration was analyzed subject to the fuel composition and combustor operating conditions listed in Reference 3. This is an adiabatic gas generator operating at 12.0 atmospheres and 1589 K TIT fired with a LBG containing 600 ppm NH_3. Figure 3 shows the adiabatic equilibrium ΣXN concentration as a function of reactant stoichiometry. ΣXN is strongly dependent upon reactant stoichiometry, and the minimum occurs at 65 percent theoretical air. On the rich side of this minimum the XN species are primarily NH_3 and HCN, whereas on the lean side the XN species are almost totally NO.

Figure 4 shows the results of kinetic calculations for a 1.0 msec ignition zone followed by a plug flow section operating at 65 percent theoretical air. Although $\Sigma(XN)$ decays toward the equilibrium value of 2.9 ppm, the rate of decay decreases with increasing residence time. For a finite primary zone residence time, both the decay rate and the equilibrium value are important. Consequently, the stoichiometry which produces minimum $\Sigma(XN)$ at equilibrium may not necessarily be the optimum stoichiometry for a combustor with limited residence time. However calculations similar to those discussed above were conducted for a range of stoichiometries and the minimum ΣXN for all residence times was found to occur with 65% theoretical air.

A secondary stage following a 65 percent theoretical air 50 msec primary stage was analyzed for two air injection patterns.

- Uniform air addition over 4.0 msec
- Uniform air addition over 60.0 msec

The results shown in Figure 5 indicate that rapid air addition gives lower emissions. Slow air addition allows the mixture to spend considerable time near stoichiometric conditions where temperatures are high. Thus, a large amount of thermal NO is formed. The decay after the peak is dilution. Full conversion of the initial 18 ppm of NH_3 would result in 8 ppm when fully diluted. The rapid air addition case produces 14 ppm which can be attributed to full conversion of the NH_3 emerging the secondary stage plus 10 ppm of thermal NO_x. The total NO_x emissions are equivalent to 14 ng/J (0.033 lb $NO_2/10^6$ Btu). Thus this combustor concept has the potential for very low NO_x emissions.

Three additional low NO_x combustor concepts are shown in Figure 6. These have been analyzed similar to the rich/lean series staged concept discussed above and the results demonstrate the potential for low NO_x emissions and certain improvements over the rich/lean series staged concept.

If the reduction of fuel XN species to N_2 is kinetically limited, the rate of reduction can be accelerated by increasing the reactant temperature (17). Concept A in Figure 6 is one way to achieve higher reactant temperatures in an overall adiabatic system. Heat is removed from the hot rich combustion products and transferred to the cooler reactants prior to ignition. The results of kinetic calculations applied to this concept show that the optimum stoichiometry for maximum XN decay shifts to richer conditions as the amount of feedback heat transfer increases. For comparable overall residence times, a combustor with 10 percent of the heat release fed back to the reactants produces NO_x emissions 16 percent lower than the simple rich/lean series staged concept.

Kinetic calculations indicate that the decrease in XN decay rate as residence time increases in a rich plug flow reactor is partially due to depletion of the radical pool from the high superequilibrium concentrations present immediately after ignition (14). By staging the air addition as in Figure 6-B, the radical pool is periodically replenished leading to a more rapid overall XN decay rate. The stoichiometry, air addition rate, and residence times can be optimized for each rich stage to achieve a minimum final XN concentration.

Ammonia conversion to N_2 might well be maximized by contacting certain species that would not normally occur in a sequential process by dividing the total combustor into two parallel streams with different stoichiometries, and then mixing the products of these two combustors prior to secondary burnout. This concept referred to as parallel staging is shown in Figure 6-C.

Although in the limit, kinetic considerations dictate the ultimate conversion of fuel nitrogen to N_2 or NO, conversions in practical systems are dictated by the realities of the fuel/air mixing process. The reactants can be premixed to ensure that reaction takes place at a single stoichiometry or the fuel and air may be supplied to the combustor separately, thus allowing reaction to take place over a range of stoichiometries which will depend upon the intensity of the mixing process. The following section describes the experimental results obtained from firing LBG in several types of combustion reactors.

SECTION 4

LOW BTU GAS COMBUSTION EXPERIMENTS

The idealized fuel/air contacting assumed in the preceeding kinetic analysis cannot be achieved in practice. The combustor designer must take account of practical constraints such as combustor cost, maintainability, and operability. Pressure drops must be minimized since they represent energy losses, and combustor volumes (and therefore, residence times) must be kept within bounds to reduce combustor cost and the potential for heat loss. The approach of this study is to use the results of kinetic analysis to guide the development of low NO_x combustion concepts primarily through experiments. This section discusses the results of a series of flame reactor experiments where LBG containing various XN compounds was combusted over a wide range of fuel/air contacting conditions. The objectives of these tests were to:

- Evaluate the relationship between LBG composition and XN processing
- Investigate XN processing in LBG-fired reactors as a function of fuel/air contacting method.

Three simple combustors were tested:

- Laminar and turbulent diffusion flame
- Premixed pseudo one-dimensional flame (flat flame)
- Premixed catalytically supported reactor

The nitrogen species included in these investigations are NH_3, HCN and NO. Hydrogen cyanide and NO were included because they are representative of the XN species which might exit a rich combustion stage, thus providing information on the optimum second stage reactor.

EXPERIMENTAL SYSTEMS

The experimental equipment used in this investigation includes:

- Reactant flow system
- Interchangeable flame reactors
- Analytical train

These components are shown schematically in Figure 7.

The LBG was synthesized by blending together high purity gases from cylinders. All gases were high purity grade (99.97 percent or better) with the exception of CO (99.0 percent). NH_3, NO and HCN were supplied as custom grade mixtures in nitrogen ($\pm$ 2 percent accuracy) to facilitate metering. The oxidant was dry air. All gases were metered with sapphire jewel orifices operated in the critical flow (sonic) regime. The pressures upstream of the orifices were measured with high accuracy variable capacitance pressure transducers which were calibrated periodically against a laboratory reference. The pressures downstream of the orifices were maintained constant and the flow rate through each orifice was calibrated by filling an evacuated tank. The estimated total inaccuracy in each gas flow rate was 0.5 percent.

Variations in water vapor content of the LBG were achieved by metering distilled water with a calibrated rotameter and prevaporizing before mixing with the other reactant gases. The mixture was maintained well above the dewpoint temperature to prevent subsequent condensation. Other design details of the reactant flow system are discussed in Reference 18.

The diffusion flame reactor utilized in these experiments is shown in Figure 8. Fuel gases entered through a stainless steel tube centered in a sintered stainless steel disc. Air passed through the sintered disc and mixed with the fuel gases by laminar or turbulent diffusion depending upon flow conditions. A fully developed velocity profile was assured by a tube length greater than 100 diameters. The surrounding tube was enclosed by a water jacket to control heat losses. Combustion products exiting the reactor were mixed by several rows of stainless steel water-cooled tubes normal to the flow. Samples were withdrawn for analysis downstream of this mixing section through a water-cooled stainless steel probe. All water cooled surfaces were maintained at 343 to 363 K.

The premixed pseudo one-dimensional flame reactor is shown in Figure 9. In this "flat flame" reactor the premixed reactants passed through a water cooled stainless steel sintered disc. Once the reactants were ignited a thin planar flame stabilized approximately 1.0 mm above the disc. The flat flame reactor was enclosed by a quartz tube and combustion products were sampled with stationary probes. The flat flame reactor was moved axially to obtain combustion product samples at any desired distance downstream from the flame front.

The premixed catalytically supported reactor is shown in Figure 10. The catalyst used in these tests was a platinum coated graded cell monolith supplied by the Acurex Corporation. The desirable features of the graded cell catalyst have been discussed previously (18). The maximum recommended temperature for this catalyst is 1588 K (2400 F). Type K thermocouples were cemented in two of the cells in the downstream segment to monitor maximum monolith temperature. To minimize heat losses and approximate adiabatic conditions, the catalyst was mounted in a refractory tube and electrically backheated. The reactants passed through a sintered stainless steel disc immediately upstream of the catalyst and combustion products were sampled with a stainless steel water cooled probe. Additional details of this reactor's construction and operation are documented in Reference 13.

The same sampling and analysis systems were used for all flame reactor studies. Combustion products were analyzed for O_2, CO, CO_2, NO, NO_x, NH_3 and HCN. The sample train components were constructed entirely of stainless steel, glass and Teflon. Ammonia and HCN were trapped by bubbling known volumes of combustion products through three water baths in series. The absorbed NH_3 and HCN concentrations were then measured by ion specific electrodes. The other product species were monitored continuously. The sample was dried to a dewpoint of 273 K in a cyclone water trap located close to the sample probe to minimize residence time between probe and trap. Nitric oxide and NO_x were measured with a Thermal Electron Corporation Model 10A chemiluminescent analyzer operated as discussed in Reference 19. NO_x concentrations were measured after the sample had passed through a stainless steel converter operated at 1073 K. This converter could not be operated under oxygen-deficient conditions because of the well-known reduction of NO.

EFFECT OF LBG COMPOSITION ON FUEL NITROGEN CONVERSION

The experiments involving the effect of LBG composition on the formation of fuel NO_x were carried out in the diffusion flame and flat flame reactors. The experimental procedure was to fire the reactors with and without an XN dopant and to calculate the percentage conversion of the dopant to XN as follows:

$$\begin{pmatrix}\text{Conversion of}\\ \text{dopant to XN}\\ (\%)\end{pmatrix} = \frac{\begin{pmatrix}\text{XN measured}\\ \text{with dopant}\\ \text{(ppm dry)}\end{pmatrix} - \begin{pmatrix}\text{XN measured}\\ \text{without dopant}\\ \text{(ppm dry)}\end{pmatrix}}{\begin{pmatrix}\text{XN calculated for full}\\ \text{conversion of dopant}\\ \text{(ppm dry)}\end{pmatrix}}$$

For experiments at fuel-lean stoichiometries, only NO and NO_x were measured. For experiments at fuel-rich stoichiometries, NO, NH_3 and HCN were measured and ΣXN was calculated as the sum. For rich experiments the XN measured without the dopant was negligible and for lean experiments, thermal NO_x was typically 50 ppm while full conversion of the dopants was usually a factor of 20 higher.

Figures 11, 12 and 13 show the results for a laminar diffusion flame. All data refer to a constant fuel volumetric flow rate, 366 K fuel and air preheat and 150 percent theoretical air. The presence of hydrocarbon fuel in the LBG was found to have the most significant effect upon the conversion of NH_3 to fuel NO_x (see Figure 11). Without methane (CH_4), percentage conversions were typically 5 percent of the dopant. This rapidly increased to greater than 20 percent when the fuel gas contained 5 percent CH_4. Above this concentration further increases in CH_4 content did not have a significant effect upon fuel fuel nitrogen conversion. The influence of ethylene (C_2H_4) as the hydrocarbon fuel is similar to that of CH_4; however, maximum conversions are lower typically of the order of 20 percent for an LBG containing 10 percent C_2H_4. It can also be seen in Figure 11 that the influence of CO/H_2 ratio was minimal compared to that of the presence of a hydrocarbon. Similar experiments varying the diluent composition to include N_2, CO_2 and H_2O showed diluent composition effects to be on the same order as CO/H_2 ratio effects (12).

The partial products of combustion of the first stage in a staged heat release combustor can contain several nitrogenous species (NO, NH_3 and HCN) as well as CO, H_2 and a hydrocarbon fuel. The results in Figure 12 show that the conversion of a given nitrogenous specie in an LBG fuel is not only dependent upon the hydrocarbon fuel content, but also on the nature of the fuel nitrogen specie. High conversions of small quantities of HCN and NO were measured for small dopant concentrations, and these conversions were almost independent of hydrocarbon content. However, at the same dopant level the conversion of NH_3 is strongly affected by hydrocarbon content.

Figure 13 shows the effects of hydrocarbon fuel concentration and dopant level on NH_3 and NO conversion. With the exception of NO as the dopant and zero percent CH_4, percentage conversion of dopants decreased as the dopant levels increased. However, this decrease in conversion was insufficient to counter the increase in XN available for conversion and total NO_x emissions increased with dopant level. At NO dopant levels greater than 500 ppm there was a significant influence of hydrocarbon content upon fuel nitrogen conversion (NO to NO_x). This suggests that if the effluents of a rich primary contained a hydrocarbon fuel gas and NO, as the only bound nitrogen species, significant reductions in emissions might be achieved in a lean secondary burnout stage.

Figure 14 shows the results of similar experiments varying CH_4 concentration in LBG-fired flat flames. The conversion of NH_3 to NO is essentially the same with and without CH_4 except at very rich conditions where some HCN is formed in the case with CH_4.

The effect of a hydrocarbon fuel on the conversion of NH_3 to NO can be explained by consideration of the reactions shown in Table 2. In a laminar diffusion flame NH_3 breakdown occurs on the fuel-rich side of the heat release zone, and N_2 formation can occur by reaction of the nitrogenous fragments. Any NO that is produced can react with these nitrogen fragments producing N_2. When a hydrocarbon fuel is present hydrogen cyanide can be produced from NO via reactions such as 7 and 8, thus effectively removing nitrogen specie from the zone in which they can be more easily converted to N_2. Once HCN is produced, then the XN specie exchange reactions allow the regeneration of NO as O_2 diffuses into the reaction zone.

In the flat flame the reactants are premixed and NH_3 breakdown occurs in the presence of O_2. Thus NH_3 and the resulting fragments compete with the fuel species for O_2. Reduction reactions are not favored. At very rich stoichiometries much less O_2 is available and the effects of hydrocarbon content become more pronounced.

It is well-known that the fuel/air contacting conditions in a diffusion flame are dependent upon fuel and oxidant flow rates. For a simple coaxial system such as the one tested here, a laminar flame is produced at low flow rates. As the flow rate is increased there is a transition to a turbulent flame with noticeable audible noise and a brush-liek appearance. As the flow rate is increased further, the flame lifts off the port allowing partial premixing of fuel and air beneath the reaction zone. Figure 15 shows the conversion of NH_3 to NO_x in LBG-fired diffusion flames operated in all three fuel/air contacting conditions.

Under laminar conditions, the hydrocarbon content is an important variable as discussed previously. Under attached turbulent conditions the conversion increases somewhat but the strong effect of CH_4 concentration is similar to the laminar case. However, in the lifted condition the effect of CH_4 disappears and conversion is nearly complete. Thus from a fuel nitrogen perspective the attached laminar and turbulent flame produces fuel nitrogen conversion similar to a premixed system.

EFFECT OF COMBUSTOR CHARACTERISTICS ON FUEL NO_x FORMATION

The effect of combustor characteristics on fuel NO_x formation was measured by firing an NH_3 doped LBG in the three reactors described previously over a range of reactant stoichiometries. The LBG composition synthesized for these tests is listed below:

CO	20 percent
H_2	20 percent
CH_4	5 percent
N_2	55 percent
NH_3	471 ppm

The heating value of this gas is 37 x 10^3 J/m^3 (182 Btu/ft^3).

Measured concentrations of NO, NH_3 and HCN are presented in Figure 16 for the diffusion flame, the premixed catalytic reactor and the premixed flat flame reactor operating fuel-rich. For the diffusion flame and catalytic reactors, combustion products were sampled downstream of the mixing device described previously. For the flat flame reactor combustion products were sampled on the axis approximately 45 msec from the primary reaction zone. Axial probing traverses showed no significant variation in these concentrations over a product residence time range of 2 to 50 msec.

The results in Figure 16 are similar for all reactors: as the percentage of theoretical air in the reactants decreased, the concentration of NO in the reactants decreased, the concentration of NO in the products decreased while the NH_3 and HCN concentrations increased. The diffusion flame utilized for these tests incorporated a water-cooled housing. As the percent theoretical air was reduced from overall lean conditions the flame expanded toward the cooled walls. Under rich conditions the base of the diffusion flame operated in the normal fashion with a near stoichiometric flame front, but the upper portion was quenched along the cold walls. This accounts for the high NH_3 throughput under rich conditions.

For the premixed catalytic reactor the HCN concentration was virtually zero down to 70 percent theoretical air. As the percent theoretical air was further decreased, HCN increased rapidly until at 45 percent theoretical air the measured NH_3 and HCN concentrations were the same. In the premixed flat flame NH_3 concentrations were very low, and the HCN concentration increased as the percentage theoretical air decreased. The NO concentrations in the premixed flat flame were generally higher than those in either of the other two reactors.

SECTION 5

DISCUSSION AND CONCLUSIONS

The results presented in this paper represent the initial portion of a study to develop combustor concepts to minimize NO_x emissions from LBG fired combined cycle power systems. Low Btu fuel gases may contain up to 3800 ppm NH_3 and this could result in high NO_x emissions under typical gas turbine combustor operating conditions. However it is known that the conversion of NH_3 to NO can be restricted by modifying the combustion process in such a way as to ensure that the NH_3 reacts initially under fuel-rich conditions. Kinetic analysis of idealized combustors has shown the potential for very low NO_x emissions even with high NH_3 concentration in the LBG.

Before the development of bench-scale combustors can commence it is necessary to ascertain the parameters controlling fuel NO_x formation in the LBG-fired systems. LBG fuel gases will vary in composition depending upon the gasifier design and operating parameters. Thus, if the combustor concepts are to be universally applicable then it is necessary to establish whether the combustor must be tailored to the particular fuel gas being produced. The results indicate that by far the most significant effect of LBG composition on fuel NO_x formation is the presence of a hydrocarbon gas.

Kinetic considerations suggest that optimum temperature/stoichiometry histories exist to maximize N_2 production. However, practical considerations require that the fuel and oxidant be mixed either before or after injection into the reaction chamber, thus providing the potential for different types of combustors based upon the fuel/air contacting process in the primary zone. A series of simple reactor experiments have been carried out with synthesized LBG to determine the influence of combustion characteristics on the processing of NH_3 in LBG. Figure 17 compares the ΣXN (measured rich) and NO_x (measured lean) for the three reactors firing the baseline LBG doped with NH_3 and similar data for the diffusion flame reactor firing an LBG with no hydrocarbons. For the baseline LBG containing CH_4, the diffusion flame and catalytic reactors produce comparable minimum conversions and the flat flame reactor produces much higher conversion over the range of stoichiometries tested. (It could not be operated richer than 60 percent theoretical air due to flame instability.) It is difficult to compare the three reactor types since their operational characteristics are different. The maximum operating temperature of the catalyst was 1588 K, and the undiluted reactants could not be burned between 40 and 230 percent theoretical air. Therefore, to obtain the results shown in Figures 16 and 17 it was necessary to dilute the reactants with nitrogen to ensure that this maximum temperature was never exceeded. In a real system this would require recirculation of cooled combustion products or heat loss from the primary section. Fenimore et al. (20) have carried out similar diffusion flame experiments and have shown that as the flame becomes turbulent there is a pronounced increase in fuel nitrogen conversion to NO_x. In the experiments reported here, the transition from laminar to turbulent flames did not produce comparable results. This can be explained only if it is accepted that at these turbulence levels the turbulent flame front provides a continuous reaction zone around the fuel stream. If turbulent levels were increased to such levels that the reaction zone were stretched and extinguished then fuel oxidant mixing could take place without reaction and the subsequent formation of fuel NO_x would increase.

REFERENCES

1. Evaluation of Phase 2 Conceptual Designs and Implementation Assessment Resulting from the Energy Conversion Alternatives Study (ECAS), prepared under Interagency Agreement E(49-18)-1751, NASA Report No. TM X-73515.

2. Shaw, H., A. E. Cerkanowicz, and S. E. Tung. Environmental Assessment of Advanced Energy Conversion Technologies - Interim Report, Vol. 1, State-of-the-Art. Contract No. 68-02-2146, U. S. Environmental Protection Agency, Cincinnati, Ohio, 1977.

3. Harris, L. P., and R. P. Shah. Energy Conversion Alternatives Study (ECAS), General Electric Phase II Final Report: Vol. II, Advanced Energy Conversion Systems - Conceptual Designs: Part 3, Open Cycle Gas Turbines and Open Cycle MHD, General Electric Report No. SRD-76-064-2, NASA Report No. NASA CR-134949, 1976.

4. Beecher, D. T., et al. Energy Conversion Alternative Study (ECAS), Westinghouse Phase II Final Report: Vol. II - Combined Gas-Steam Turbine Plant Using Coal-Derived Fuel, Westinghouse Report No. 76-9E9-ECAS-R2v.2, NASA Report No. NASA CR-134942, 1976.

5. Fluor Engineers and Constructors, Inc. Gasification-Combined-Cycle Power Plants. EPRI Journal, July/August, 1978. p. 43.

6. Robson, F. L., W. A. Blecher, and A. J. Giramonti. Combined-Cycle Power Sytems. EPA-600/2-76-149, U. S. Environmental Protection Agency, Washington, DC, 1976. p. 359

7. Environmental Protection Agency Title 40, Chapter 1, Subcharter C, Part 60-Standards of Performance for New Stationary Sources, Federal Register, Vol. 36, No. 247, December 23, 1971.

8. Tyson, T. J., M. P. Heap, C. J. Kau, B. A. Folsom, and N. D. Brown. Low NO_x Combustion Concepts for Advanced Power Generation Systems Firing Low Btu Gas. EPA-600/2-77-235, U. S. Environmental Protection Agency, Washington, DC, 1977.

9. Dravo Corporation, Handbook of Gasifiers and Gas Treatment Systems, NTIS Report No. FE-1772-11, Feburary 1976.

10. Folsom, B.A., T. L. Corley, M. H. Lobell, C. J. Kau, M. P. Heap, and T. J. Tyson. Evaluation of Combustor Design Concepts for Advanced Energy Conversion Systems. In: Proceedings of the Second Stationary Source Combustion Symposium, Vol. 5, Addendum, EPA-600/7-77-073, July 1977.

11. Heap, M. P., T. J. Tyson, J. E. Cichanowicz, R. Gershman, and C. J. Kau. Environmental Aspects of Low Btu Gas Combustion. In: Sixteenth Symposium on Combustion, The Combustion Institute, 1977. p. 535.

12. Folsom, B. A., C. W. Courtney, M. P. Heap, and G. B. Martin. The Effect of LBG Composition and Combustor Characteristics on Fuel NO_x Formation. In: Fourteenth Annual International Gas Turbine Conference, A.S.M.E., Gas Turbine Division, March 1979.

13. Folsom, B. A., C. W. Courtney, and M. P. Heap. Environmental Aspects of Low Btu Gas-Fired Catalytic Combustion. Proceedings of the Third Workshop on Catalytic Combustion, October 3-4, 1978.

14. Tyson, T. J., et al. Fundamental Combustion Research Applied to Pollutant Control. First Annual Report, EPA Contract 68-02-2631. In preparation.

15. Morley, C. The Formation and Destruction of Hydrogen Cyanide from Atmospheric and Fuel Nitrogen in Rich Atmospheric-Pressure Flames. Combustion and Flame, Vol. 27, 1976. pp. 189-204.

16. Myerson, A. L. The Reduction of Nitric Oxide in Simulated Combustion Effluents by Hydrocarbon-Oxygen Mixtures. Fifteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, 1975.

17. Sarofim, A. F., J. H. Pohl, and B. R. Taylor. Mechanisms and Kinetics of NO_x Formation Recent Developments. Paper presented at 69th Annual Meeting AIChE, Chicago, November 1976.

18. Kesselring, J. P., W. V. Krill, and R. M. Kendall. Design Criteria for Stationary Source Catalytic Combustors. EPA-600/7-77-073c, U. S. Environmental Protection Agency, Washington, DC, July 1977. p. 193.

19. Folsom, B. A., and C. W. Courtney. Chemiluminescent Measurement of Nitric Oxide in Combustion Products. In Proceedings of the Third Stationary Source Combustion Symposium, March 1977.

20. Fenimore, C. P. Effects of Diluents and Mixing on Nitric Oxide from Fuel Nitrogen Species in Diffusion Flames. Seventeenth Combustion Symposium, published by the Combustion Institute, 1978. p. 1065.

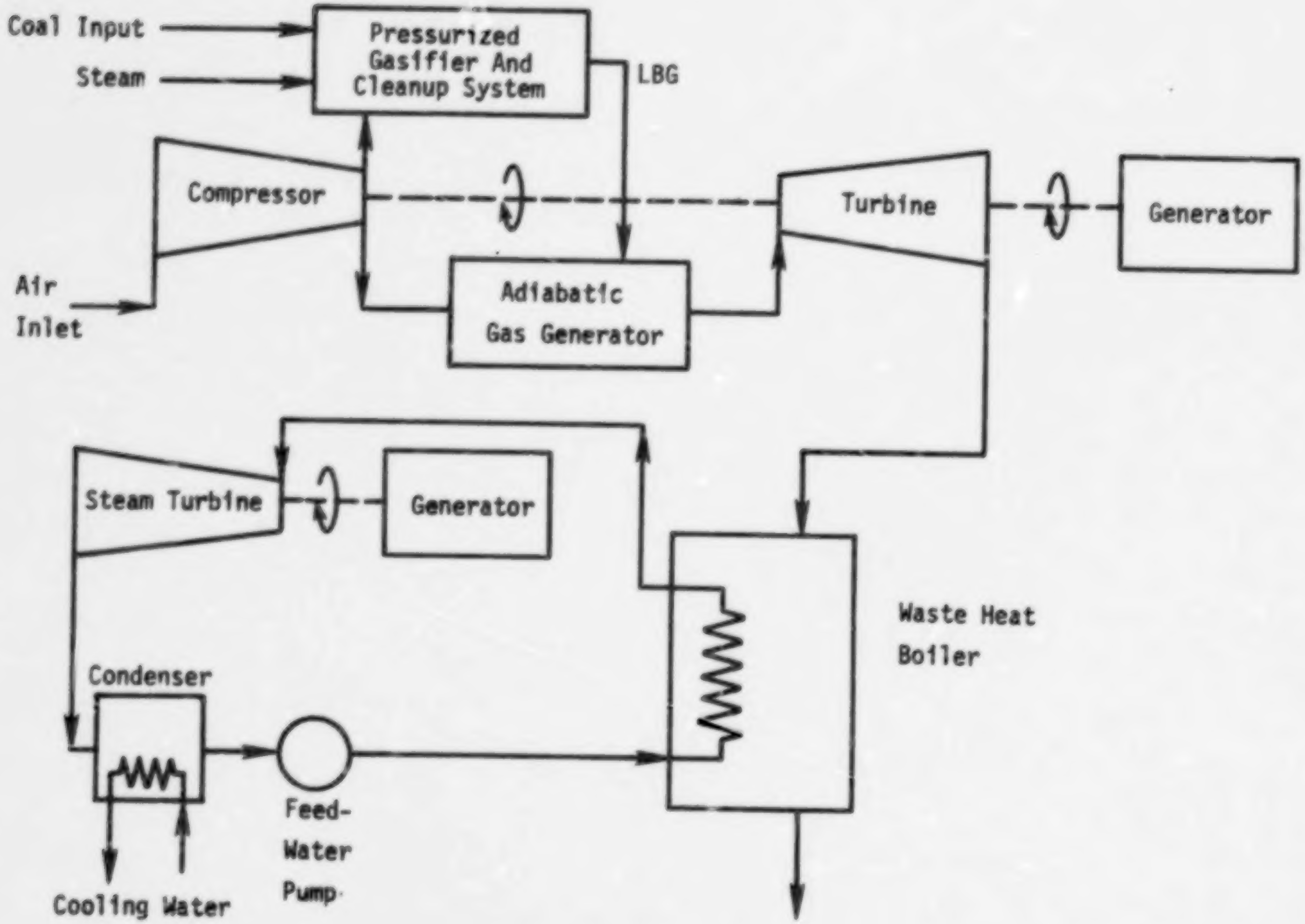

Coal Input
Steam
Pressurized Gasifier And Cleanup System
LBG
Compressor
Turbine
Generator
Air Inlet
Adiabatic Gas Generator
Steam Turbine
Generator
Waste Heat Boiler
Condenser
Feed-Water Pump
Cooling Water

Figure 1. Simplified Schematic of Basic LBG-Fired Combined Cycle.

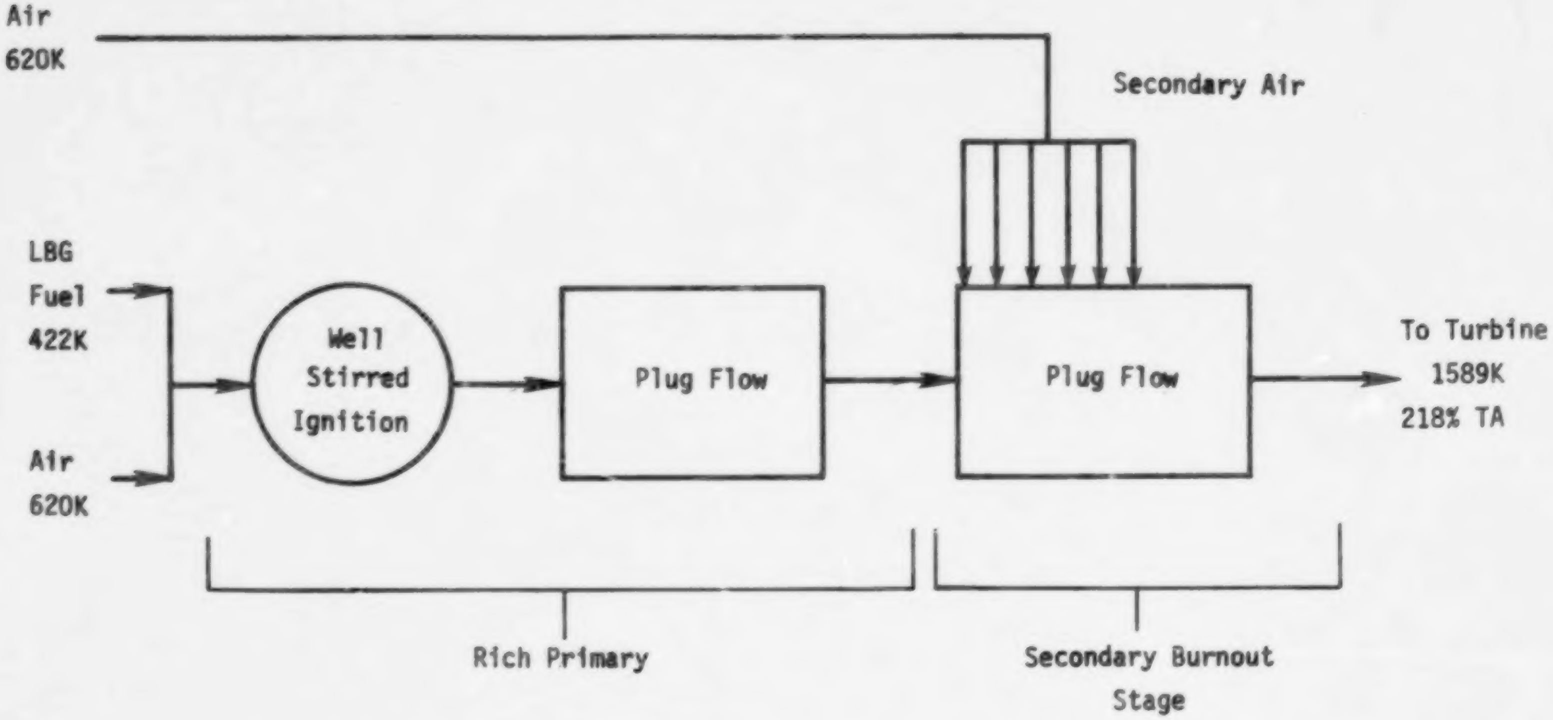

Air
620K
Secondary Air
LBG
Fuel
422K
Air
620K
Well
Stirred
Ignition
Plug Flow
Plug Flow
To Turbine
1589K
218% TA
Rich Primary
Secondary Burnout
Stage

Figure 2. Limit Case Schematic Diagram of a Rich/Lean Series Staged Combustor.

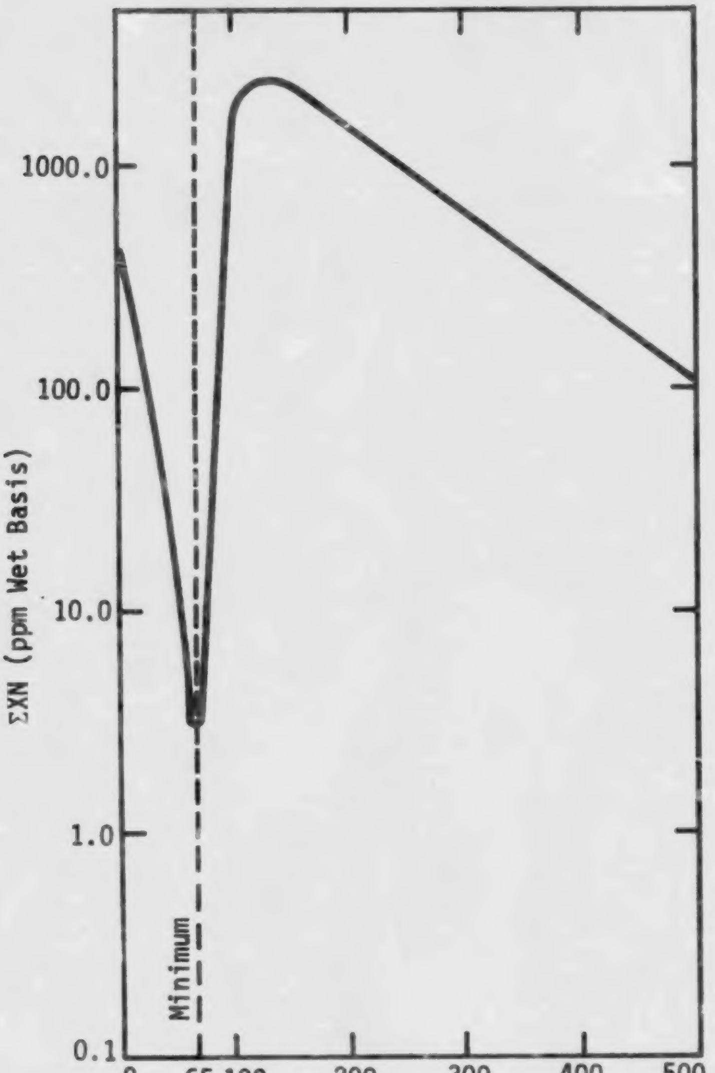


Figure 3. Adiabatic Equilibrium ΣXN for LBG.

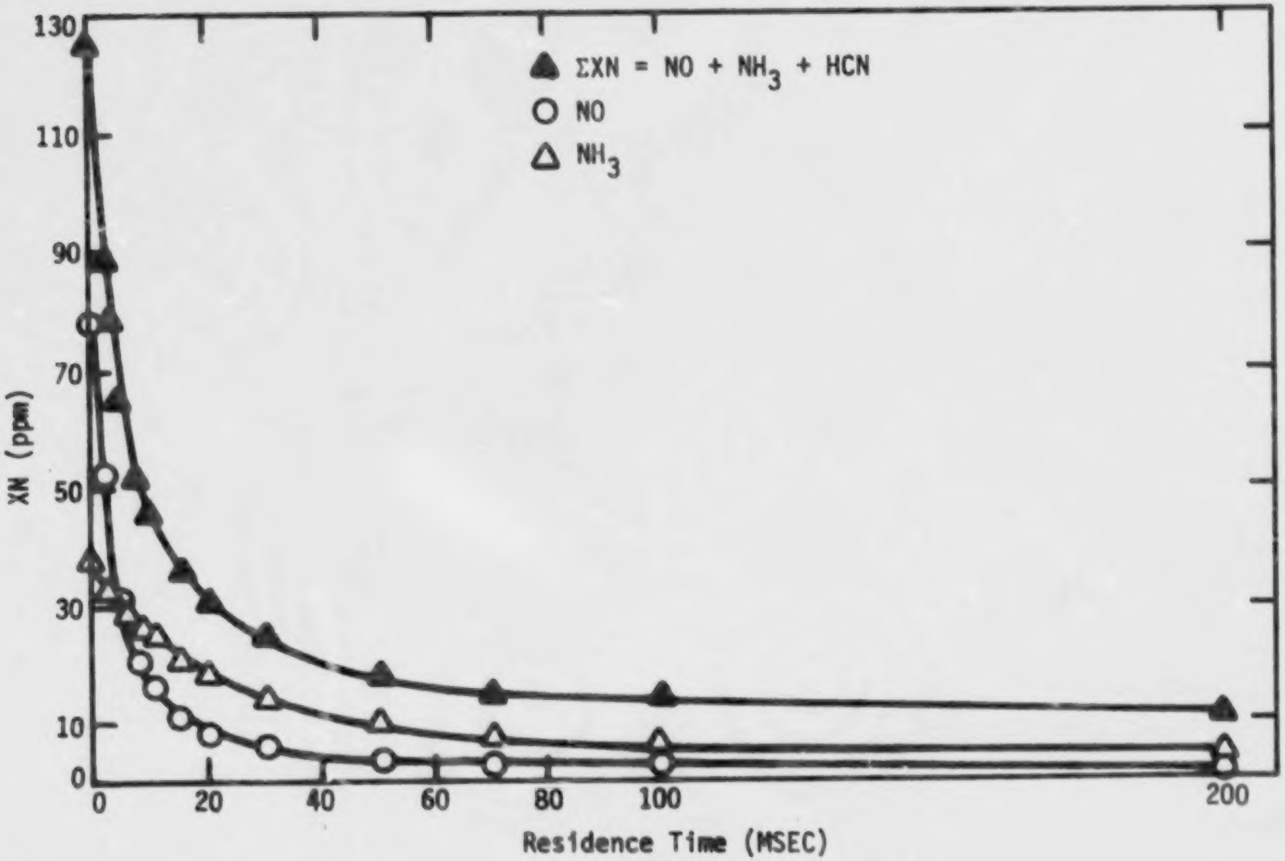


Figure 4. Kinetic Analysis of 65% Theoretical Air Rich Primary.

FIG. 3

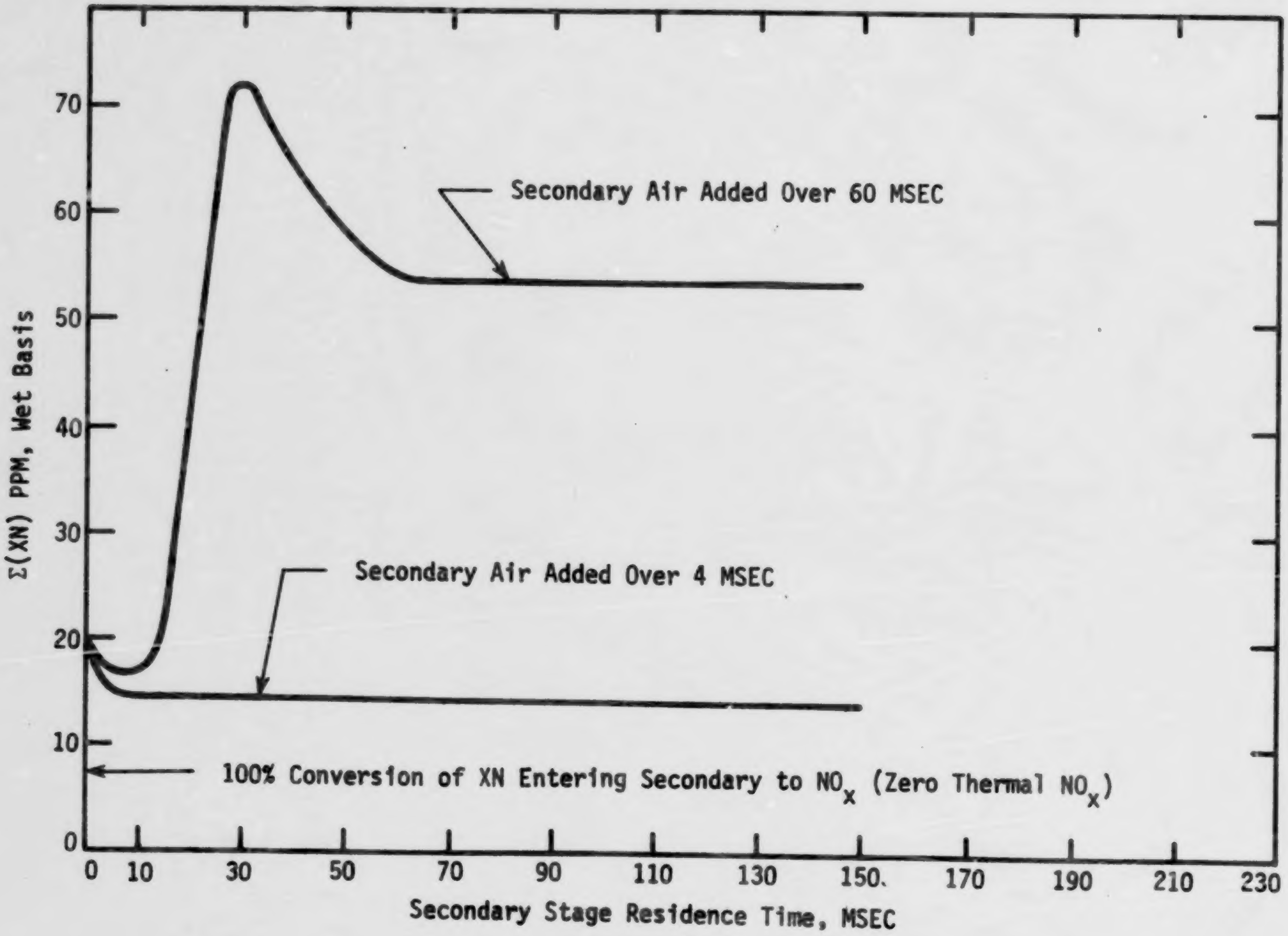
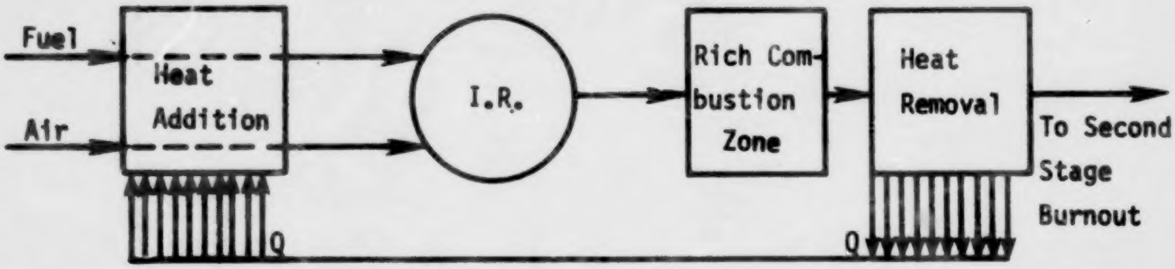
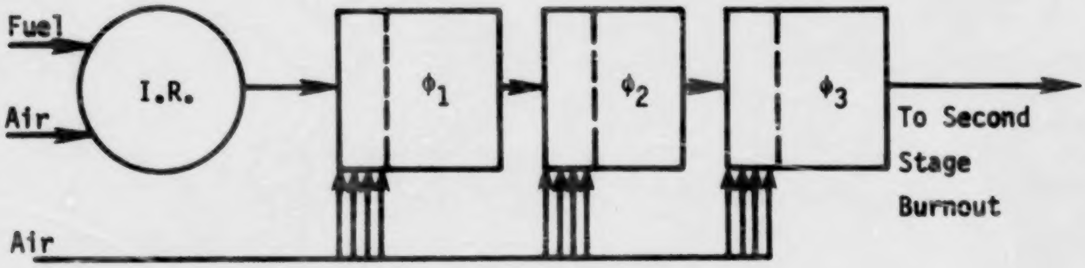


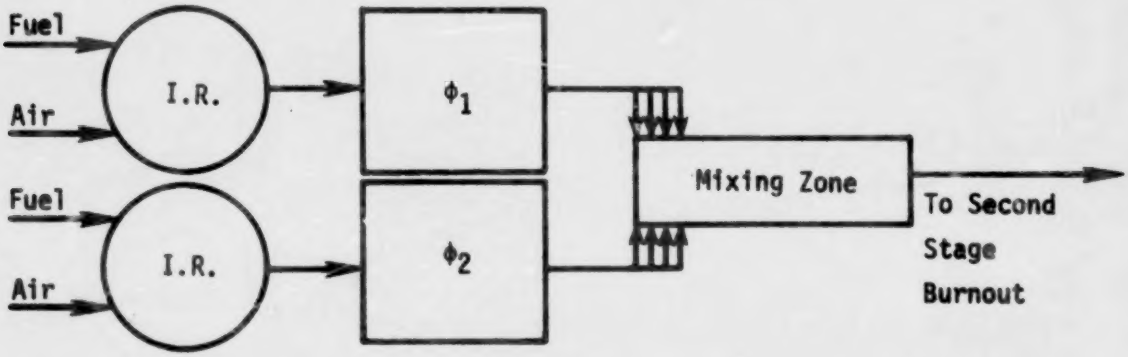
Figure 5. Second Stage Air Addition.


Fuel
Air
Heat Addition
I.R.
Rich Combustion Zone
Heat Removal
To Second Stage Burnout
Q
Q

A. Heat Feedback


Fuel
Air
I.R.
ϕ_1
ϕ_2
ϕ_3
To Second Stage Burnout
Air

B. Distributed Air Addition


Fuel
Air
I.R.
ϕ_1
Fuel
Air
I.R.
ϕ_2
Mixing Zone
To Second Stage Burnout

C. Parallel Staging $\phi_1 \neq \phi_2$

Figure 6. Idealized Low NO_x Combustor Concepts.

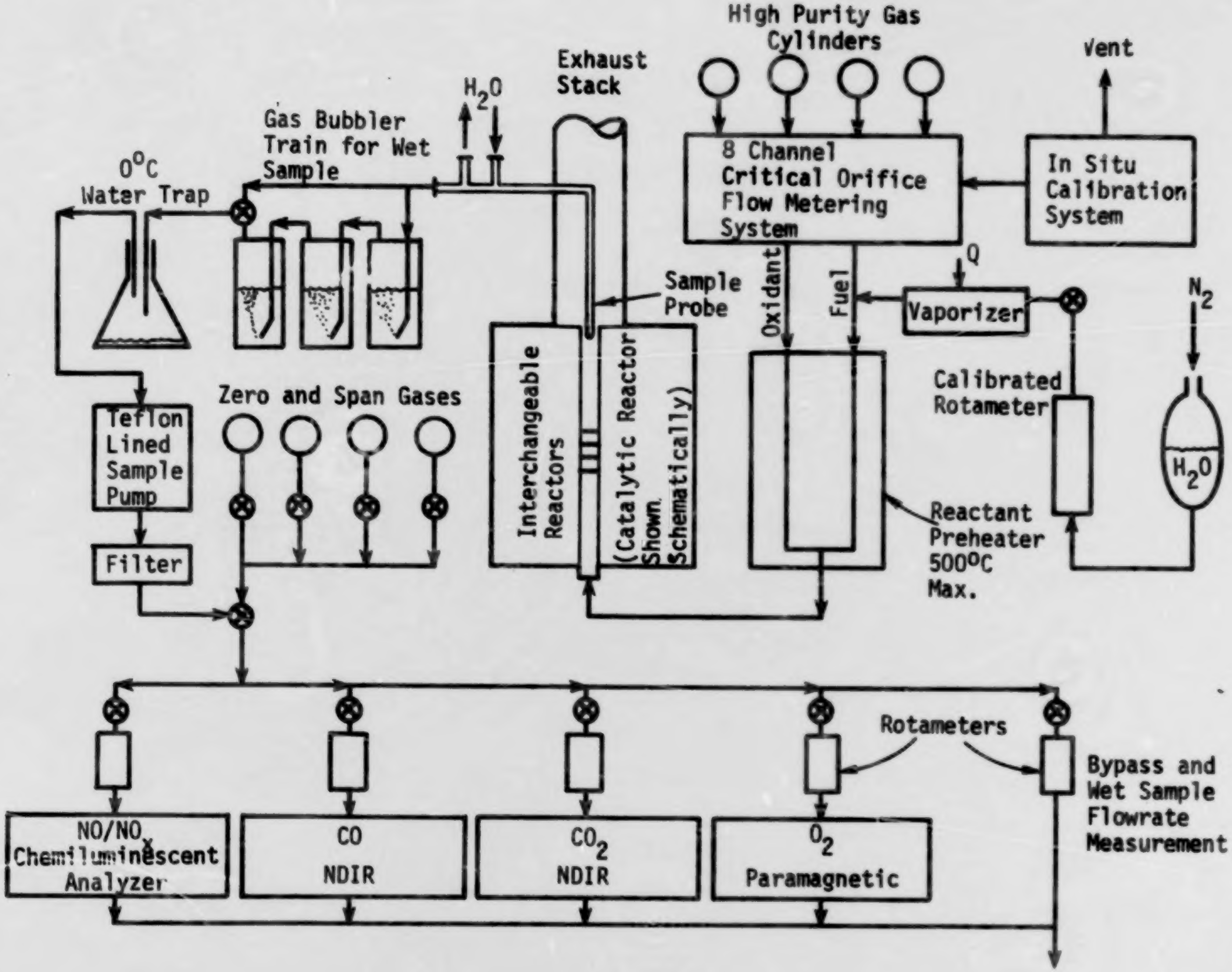

High Purity Gas Cylinders
Vent
Exhaust Stack
H_2O
Gas Bubbler Train for Wet Sample
0^oC Water Trap
8 Channel Critical Orifice Flow Metering System
In Situ Calibration System
Q
Sample Probe
Oxidant
Fuel
Vaporizer
N_2
Calibrated Rotameter
H_2O
Teflon Lined Sample Pump
Zero and Span Gases
Interchangeable Reactors
(Catalytic Reactor Shown Schematically)
Reactant Preheater 500°C Max.
Filter
Rotameters
Bypass and Wet Sample Flowrate Measurement
NO/NO_x Chemiluminescent Analyzer
CO NDIR
CO_2 NDIR
O_2 Paramagnetic

Figure 7. Experimental Apparatus.

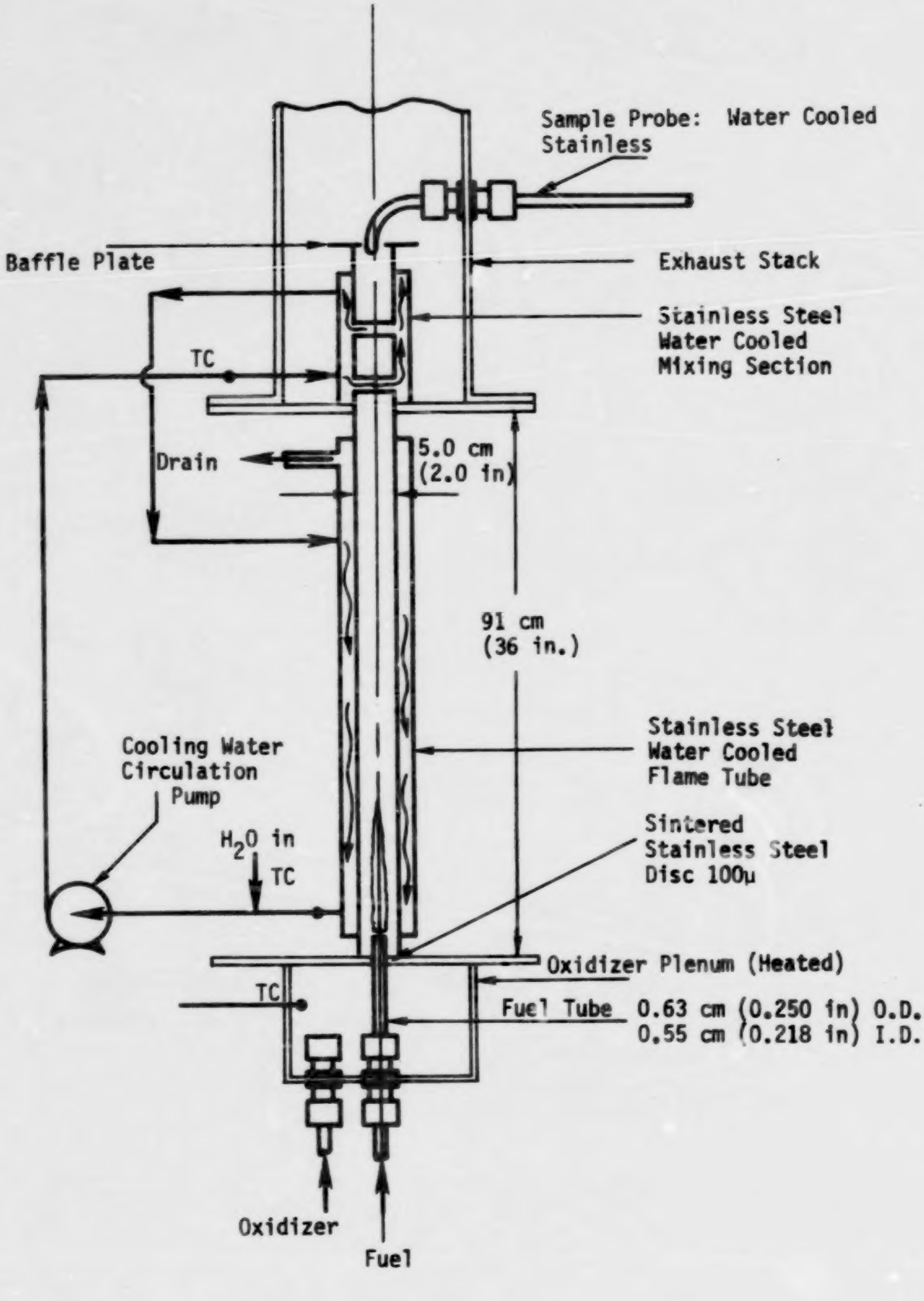

Sample Probe: Water Cooled Stainless
Baffle Plate
Exhaust Stack
Stainless Steel Water Cooled Mixing Section
TC
Drain
5.0 cm (2.0 in)
91 cm (36 in.)
Stainless Steel Water Cooled Flame Tube
Cooling Water Circulation Pump
H_2O in
TC
Sintered Stainless Steel Disc 100μ
Oxidizer Plenum (Heated)
TC
Fuel Tube 0.63 cm (0.250 in) O.D.
0.55 cm (0.218 in) I.D.
Oxidizer
Fuel

Figure 8. Diffusion Flame Reactor.

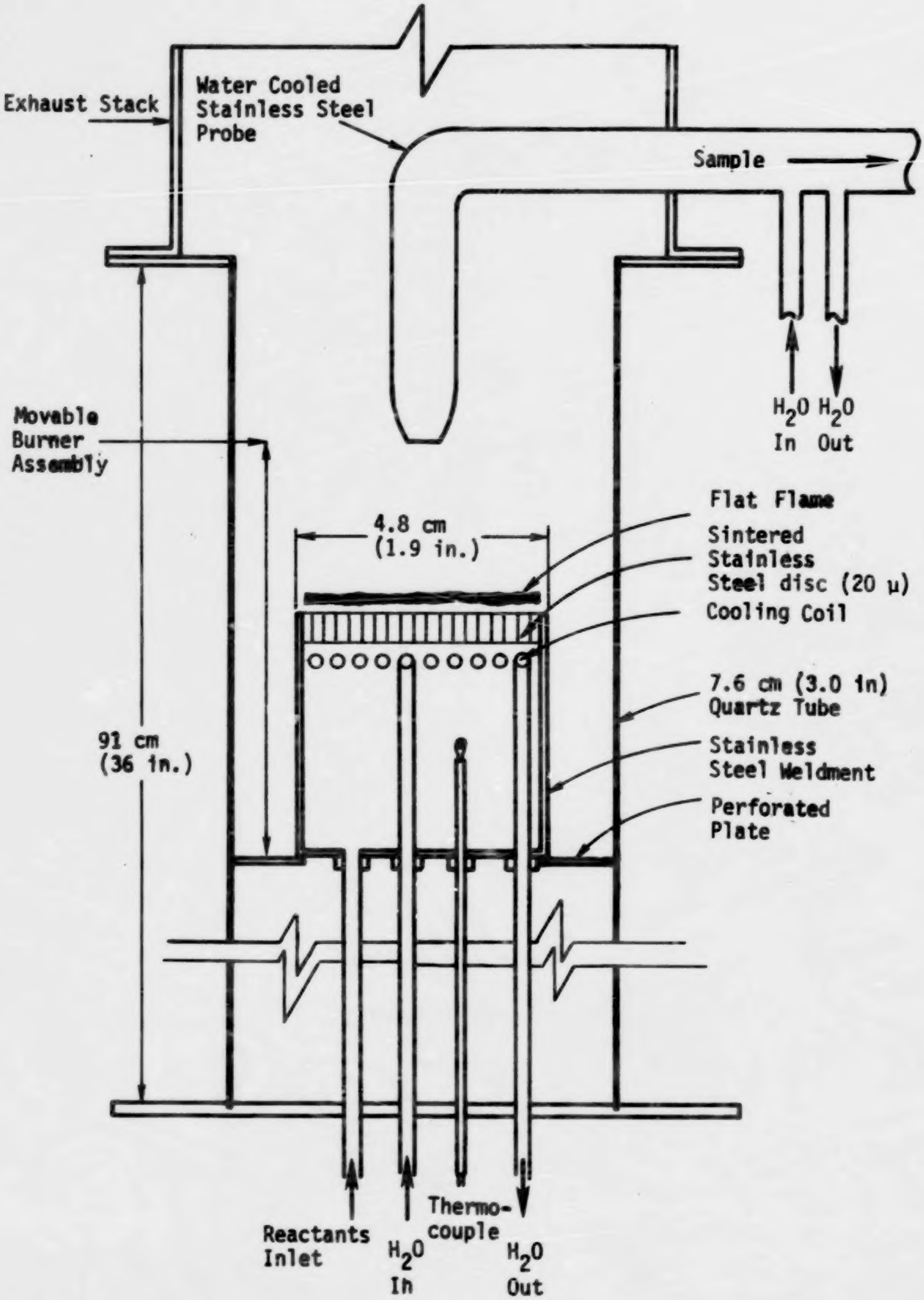

Water Cooled
Stainless Steel
Probe
Exhaust Stack
Sample
H_2O In
H_2O Out
Movable
Burner
Assembly
Flat Flame
4.8 cm
(1.9 in.)
Sintered
Stainless
Steel disc (20 μ)
Cooling Coil
7.6 cm (3.0 in)
Quartz Tube
91 cm
(36 in.)
Stainless
Steel Weldment
Perforated
Plate
Reactants
Inlet
H_2O
In
Thermo-
couple
H_2O
Out

Figure 9. Flat Flame Burner.

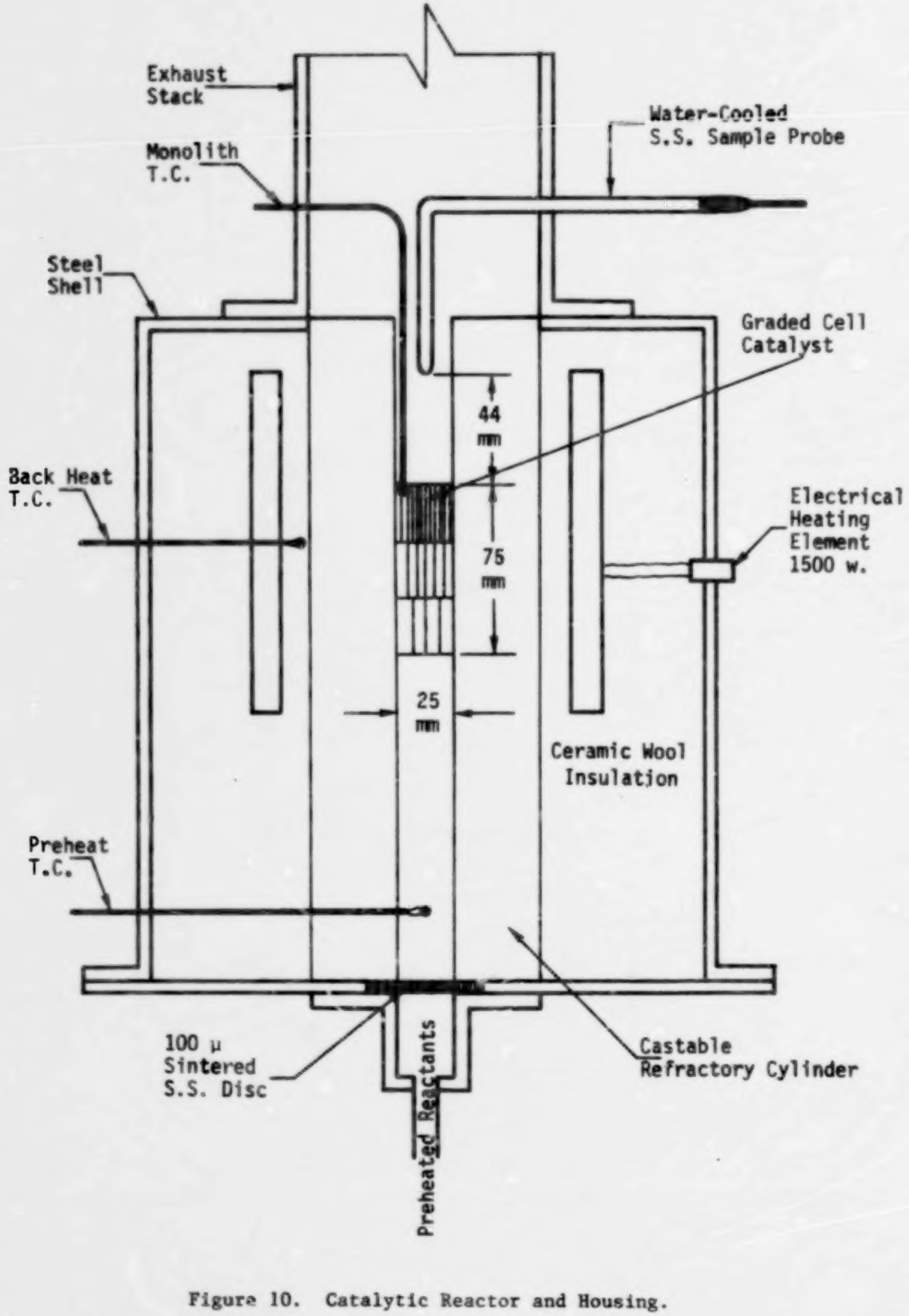

Exhaust Stack
Water-Cooled S.S. Sample Probe
Monolith T.C.
Steel Shell
Graded Cell Catalyst
44 mm
Back Heat T.C.
Electrical Heating Element 1500 w.
75 mm
25 mm
Ceramic Wool Insulation
Preheat T.C.
100 μ Sintered S.S. Disc
Castable Refractory Cylinder
Preheated Reactants

Figure 10. Catalytic Reactor and Housing.

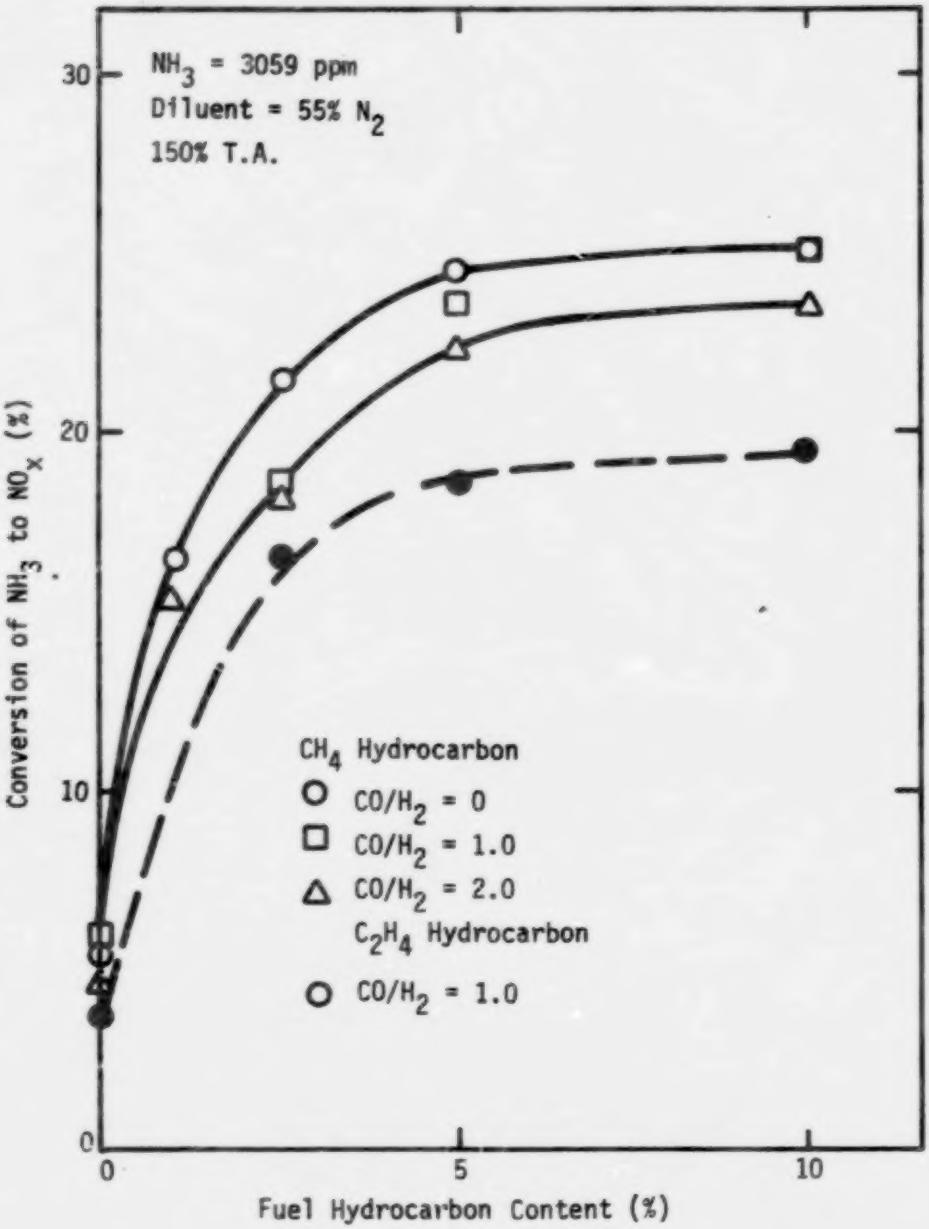


Figure 11. Laminar Diffusion Flame Processing of NH_3.

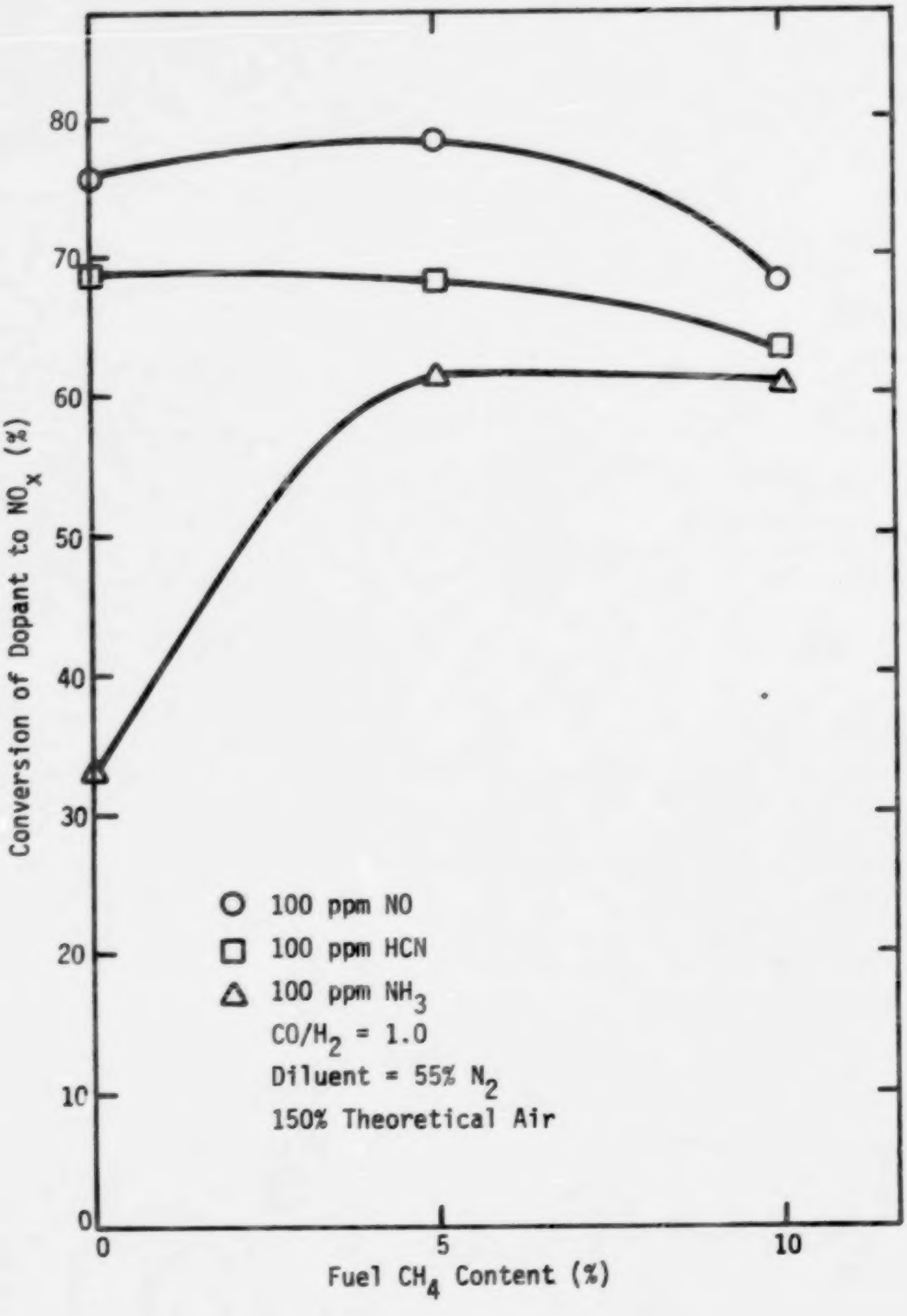


Figure 12. Diffusion Flame Processing of XN at Low Concentrations.

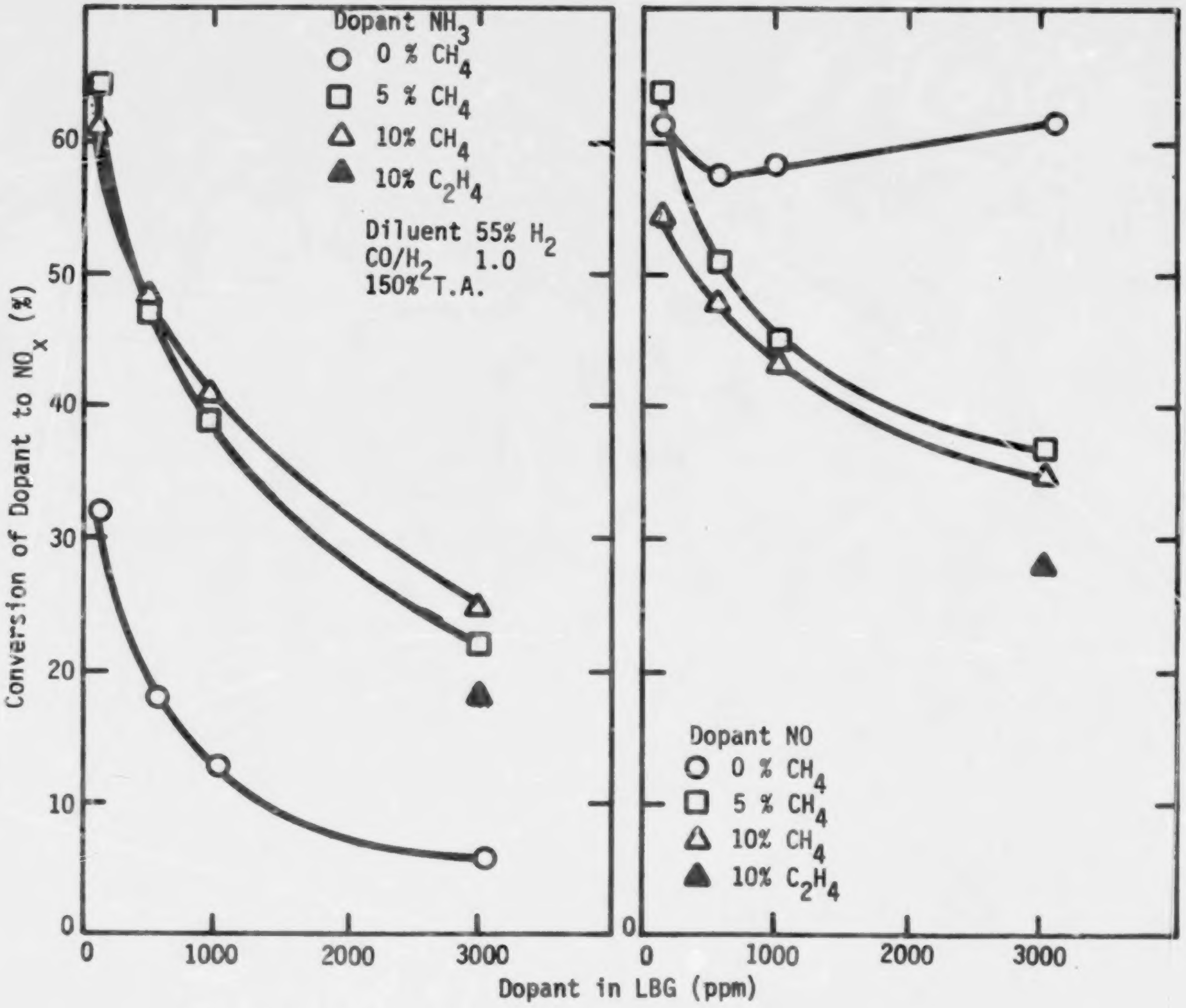


Figure 13. Laminar Diffusion Flame Process of NH_3 as Function of Dopant and Hydrocarbon Concentrations.

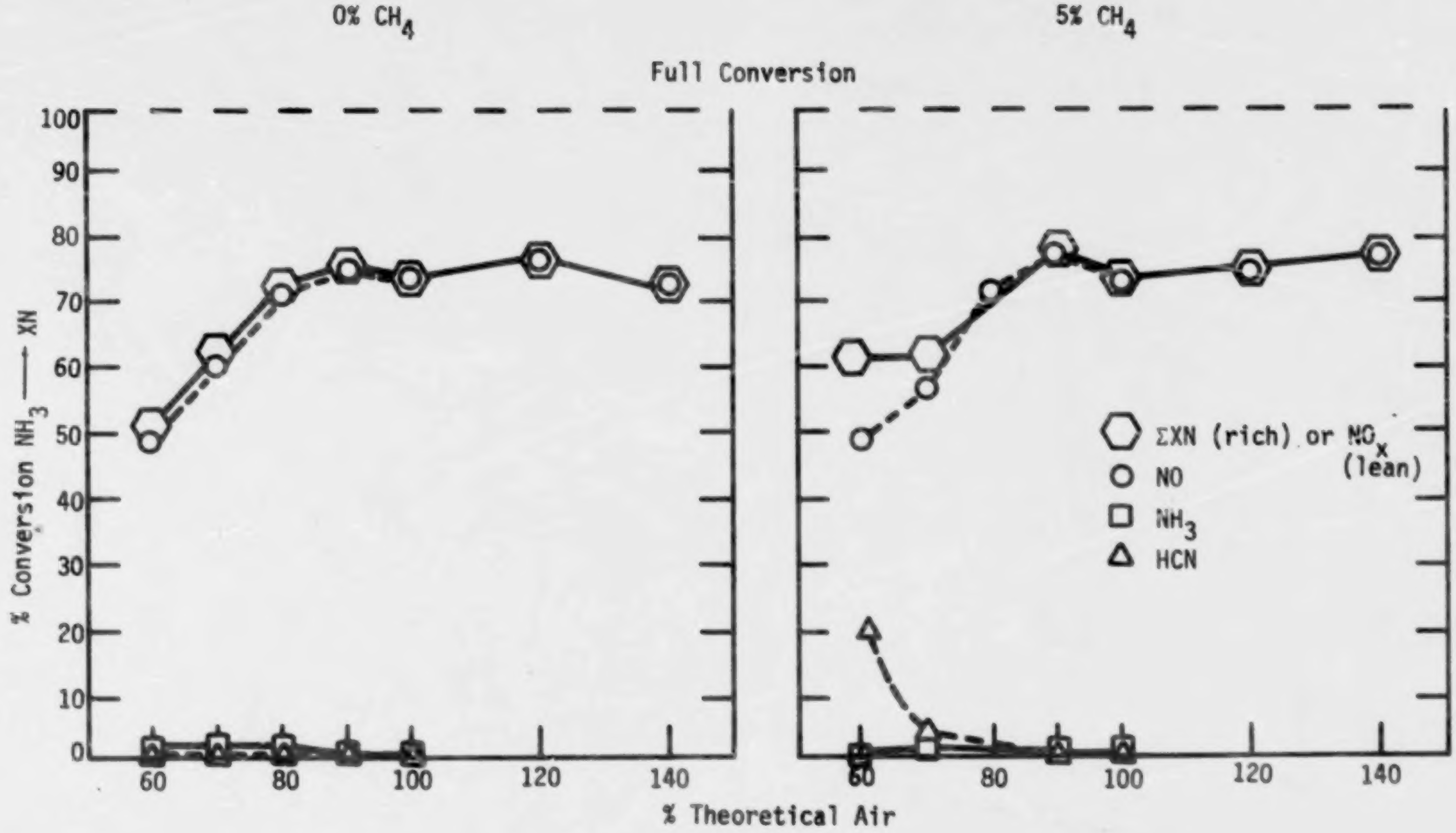


Figure 14. Flat Flame: Effects of Fuel Hydrocarbon Content on NH_3 Conversion to XN.

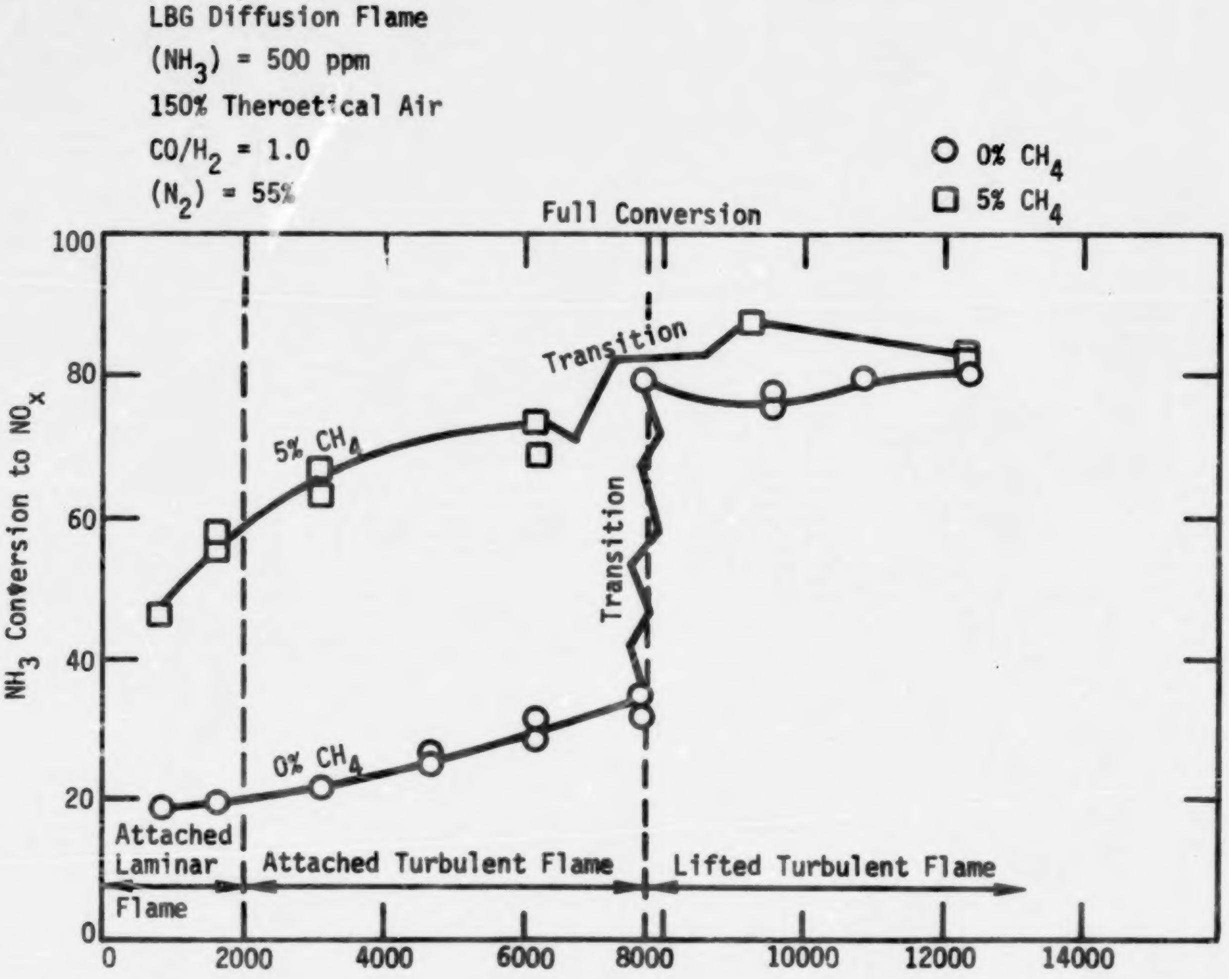


Figure 15. Diffusion Flame: Effects of Flow Characteristics on NH_3 Conversion to XN at 150% Theoretical Air.

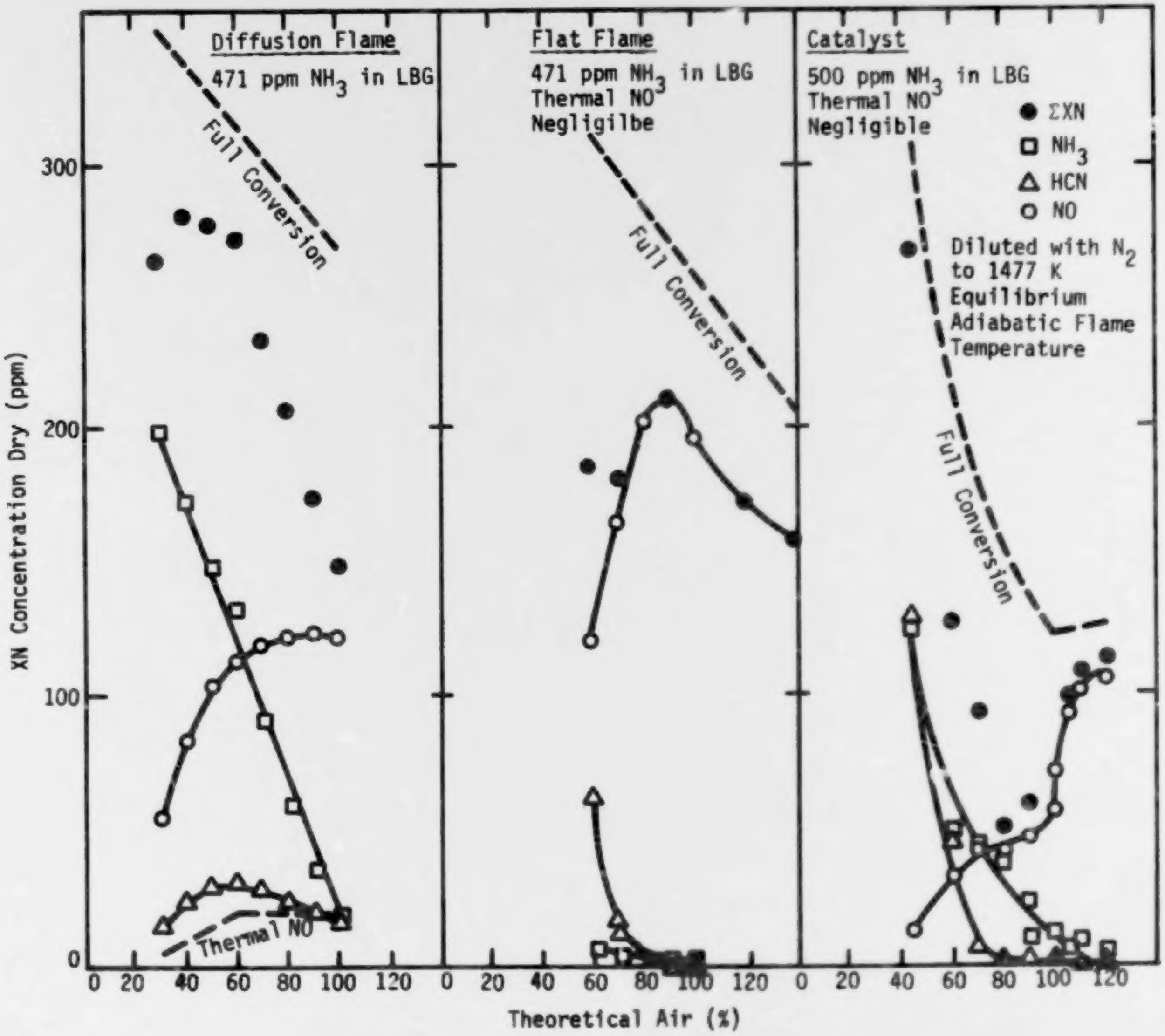


Figure 16. Comparison of XN Emissions from Three Reactors.

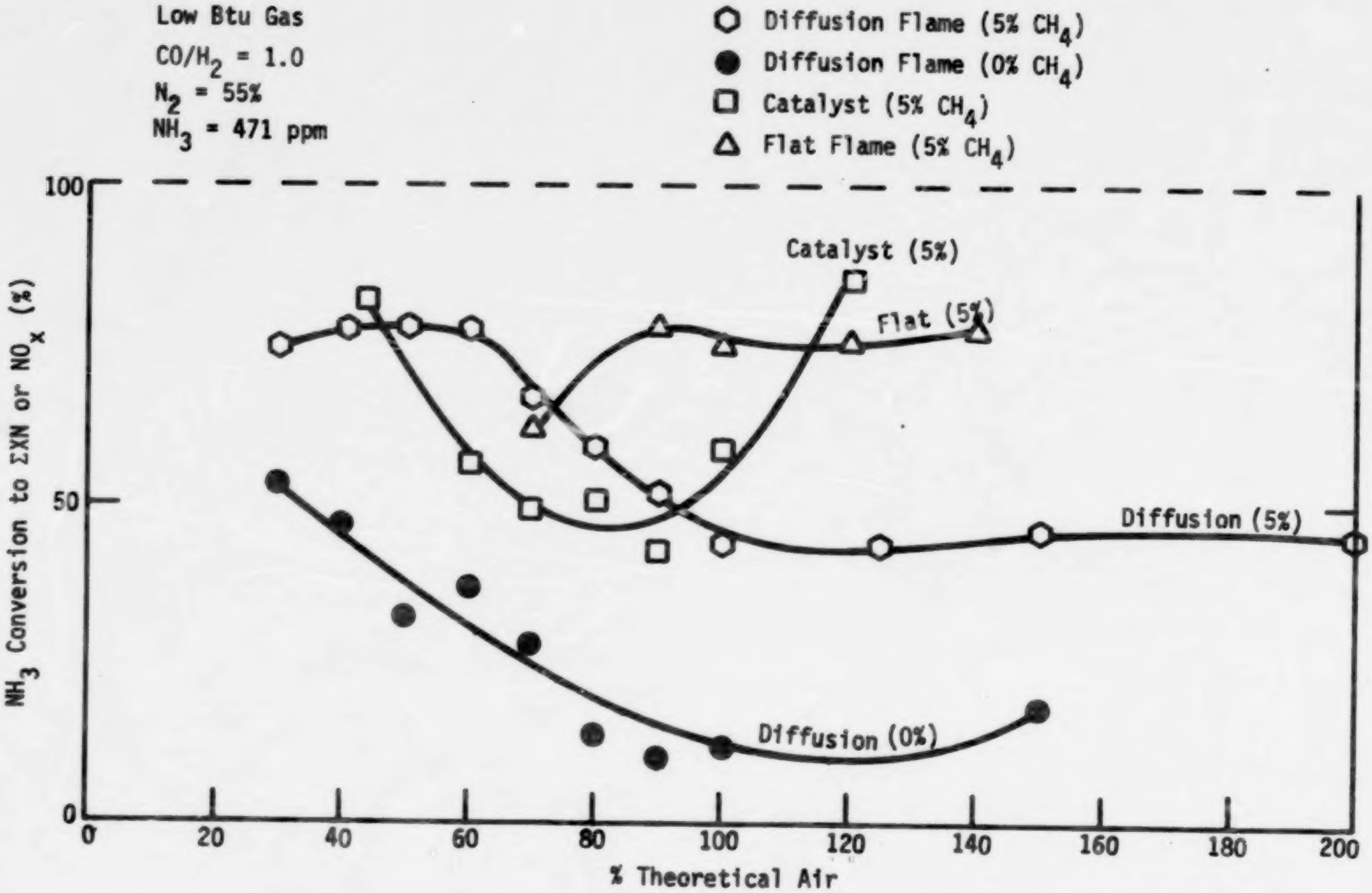


Figure 17. NH$_3$ Conversion to ΣXN for Three Reactors.

TABLE I. OVERALL EFFICIENCY AND COMBUSTOR OPERATING CONDITIONS FROM THERMODYNAMIC ANALYSIS

CYCLE/TIT (K)	OVERALL EFFICIENCY (%)	COMBUSTOR OPERATING CONDITIONS						
		TYPE*	PRESSURE (ATM)	OUTLET TEMP. (K)	OXIDANT AIR STOICH. (% TA)	OXIDANT AIR TEMP. (K)	STOICH. (% TA)	HEAT*** (%)
Basic/1366	39.1	AGG	16.0	1366	NV**	697	377	0
Basic/1700	46.3	AGG	30.0	1700	NV	844	286	0
Duct Heater/1366	40.1	AGG	16.0	1366	NV	697	377	79.3
		ADH	1.1	914	377	762	314	20.7
Duct Heater/1700	46.8	AGG	30.0	1700	NV	844	286	91.0
		ADH	1.1	914	286	840	268	9.0
Supercharged Boiler/1366	41.0	SB	16.0	1366	NV	697	309	16.3
Supercharged Boiler/1700	47.3	SB	30.0	1700	NV	844	265	6.9
Reheat/1366	44.6	AGG	20.0	1366	NV	536	425	62.3
		ARC	6.9	1366	425	1078	283	37.7

* AGG = Adiabatic Gas Generator; ADH = Adiabatic Duct Heater; SB = Supercharged Boiler; ARC = Adiabatic Reheat Combustor

** NV = Nonvitiated Air

*** For duct heater and reheat combustor, Heat % is % of total heat liberated in combustor. For supercharged boiler it is % of total heat transferred to bottom cycle.

TABLE II. MAJOR FEATURES OF KINETIC SCHEME DESCRIBING THE FATE OF AMMONIA DURING COMBUSTION

Ammonia Breakdown	
$NH_3 + H \rightarrow NH_2 + H_2$	1
$NH_2 + H \rightarrow NH + H_2$	2
$NH + H \rightarrow N + H_2$	3
Nitric Oxide Formation	
$N + O_2 \rightarrow NO + O$	4
$N_2 + O \rightarrow NO + N$	5
$N + OH \rightarrow NO + H$	6
Hydrogen Cyanide Formation	
$CH_3 + NO \xrightarrow[\text{and } CH_2NOH]{\text{via } CH_3NO} HCN + \ldots$	7
$CH + NO \rightarrow HCN + O$	8
$CH + N_2 \rightarrow HCN + N$	9
XN Specie Exchange	
$HCN + OH \rightarrow CN + H_2O$	10
$CN + OH \rightarrow NCO + H$	11
$NCO + H \rightarrow NH + CO$	12
$NH + H_2 \rightarrow NH_2 + H$	2 R
$NH_2 + H_2 \rightarrow NH_3 + H$	1 R
Nitrogen Formation	
$N + NO \rightarrow N_2 + O$	5 R
$NH_2 + NO \rightarrow N_2 + H_2O$	13

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CATALYTIC COMBUSTION SYSTEM DEVELOPMENT FOR STATIONARY SOURCE APPLICATIONS

By:
J. P. Kesselring, W. V. Krill, E. K. Chu, and R. M. Kendall
Acurex Corporation
Mountain View, California 94042

ABSTRACT

An experimental program has been conducted for the Environmental Protection Agency to develop design criteria for catalytic combustors as applied to stationary systems. The program included catalyst screening tests from which the graded cell concept was developed. The graded cell catalyst exhibits greatly enhanced combustion characteristics in terms of increased maximum throughput. Advanced testing of the graded cell catalysts showed high heat release rate capabilities with low emissions of CO, HC, and thermal NO_x. Operation of the catalysts under fuel-rich conditions showed capability to control fuel NO_x emissions. Additional criteria for system scaleup and operation under varying preheat and pressure conditions were also generated.

Catalysts developed during the program were incorporated into three small-scale systems with heat extraction. A radiative catalyst/watertube system, utilizing direct heat removal from the catalyst, was devised and tested. The concept has potential application to watertube boilers. A model gas turbine combustor was tested at pressures between 0.101 and 1.01 MPa (1 to 10 atmospheres) to investigate operating characteristics and fuel nitrogen conversion to NO_x. The final system, a two-stage combustor, was constructed to utilize fuel-rich first stage combustion for fuel NO_x control. Measured emission results make the concept attractive for a variety of future system applications.

INTRODUCTION

Catalytic combustors have shown promise in reducing the levels of CO, HC, and NO_x emissions over those of conventional burners in laboratory tests. In order to develop and later demonstrate catalytic combustors for commercially viable systems, two related development activities were performed. The first activity involved the development and characterization of catalyst systems, while the second activity focused on the analytical and experimental evaluation of three system concepts employing catalytic combustors.

The following section of this paper presents data on a variety of catalyst models with varying substrate, washcoat, and catalyst materials. This data indicates the catalyst system heat release capabilities, preheat requirements, temperature limitations, and operational life. The subsequent section presents three subscale designs and operational results for watertube boiler, gas turbine combustor, and two-stage combustion systems using catalytic combustors. The concepts, designs, analyses, and data presented here were generated under EPA Contracts 68-02-2116 and 68-02-2611, Task 11.

CATALYST DEVELOPMENT

In order to develop catalyst models for subsequent system application, a number of desirable catalyst characteristics were identified. These characteristics include:

- Low ignition temperature
- Low preheat requirements for sustained combustion
- Combustion uniformity throughout the bed
- High heat release capability
- High combustion efficiency
- Low pollutant emissions
- High operating temperature
- Fuel flexibility
- Long life

Catalyst models tested included variations in substrate, washcoat, and catalyst materials -- as well as substrate geometry and preparation techniques.

As reported at the Second Stationary Source Combustion Symposium (Reference 1), an initial series of combustion tests were performed at the Jet Propulsion Laboratory and at Acurex. Results from those tests indicated that catalyst performance was improved by:

1. Increased catalyst loading, resulting in lower initial lightoff temperatures, higher mass throughputs, and increased lifetime at 1367K (2000°F).
2. Increased cell size, allowing higher possible mass throughputs at the expense of increased hydrocarbon emissions.
3. Heavier hydrocarbon fuels which promote lightoff at lower ignition temperatures.
4. Hydrogen sulfide (H_2S) fixation of platinum catalysts to promote retention of platinum surface area.

5. Presintering of catalyst washcoats which reduces burying of active catalyst below the surface during combustion.

6. Stabilization of γ-Al_2O_3 washcoats with cesium oxide (Cs_2O) up to 5 weight percent increased surface area. Stabilization of alumina washcoats with ceria up to 5 weight percent had a negative effect on surface area.

7. Decreased cell size to significantly reduce unburned hydrocarbon and carbon monoxide emissions.

8. Catalyst beds of combined large cell and small cell monoliths also significantly increase throughput (at a given preheat temperature) and overall catalyst life with low emissions.

9. Bed temperature uniformity was increased by operation at higher temperatures.

Catalysts with combined large and small cell segments represent the best concept developed by the test series. This graded cell concept (three segments shown in Figure 1) was further developed through predictions of the PROF-HET catalytic combustion computer code (Reference 2). Finally, preliminary data with ammonia-doped natural gas indicated a potential for control of fuel nitrogen compounds to NO_x under lean conditions.

GRADED CELL CATALYST TESTS

Additional catalyst screening tests were conducted at Acurex on the graded cell configuration. The primary objective of these tests was to identify the best catalysts for system application. Catalysts were also tested for high temperature capability, system scaleup design criteria, and conversion data of fuel nitrogen to nitrogen oxides under varying operating conditions.

Screening catalysts were obtained from six sources, including W. R. Grace and Company, Universal Oil Products, Inc., William Pfefferle (a private consultant), Matthey Bishop, Inc., Johnson Matthey, and Acurex. Substrate materials were either DuPont alumina or Corning zirconia spinel. Washcoats varied from proprietary preparations with high pretest surface area to no washcoat with low pretest surface area. Catalysts were either precious metal, metal oxide, or mixtures. The catalyst loadings and fuels used are listed in Table I.

To support combustion test results, pre- and post-test catalyst physical measurements were made. These measurements included catalyst surface area and dispersion performed in the EPA/Acurex catalyst characterization laboratory. Additional scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (EDAX) tests were performed at the Jet Propulsion Laboratory as required. Table II is presented for reference, and summarizes all surface area and dispersion measurements.

Catalysts were aged for 10 hours and compared in maximum throughput, varying stoichiometry, and minimum preheat tests. Some catalysts, primarily precious metals with low loadings, exhibited lifetimes of less than 10 hours, precluding extensive data evaluation. Others were tested in a complete 20 to 30 hours test sequence. In addition, some catalysts showed preferential activity for either fuel-rich or fuel-lean combustion or for operation only at higher preheats of 700K to 811K (800°F to 1000°F).

The maximum throughput (volumetric heat release rate) capabilities were compared for various graded cell catalysts to indicate relative activity. Catalyst data selected from Table I are compared below.

MAXIMUM THROUGHPUT COMPARISON DATA**

Catalyst Type	Manufacturer	T_{Bed} K	SV, 1/hr	$q''', \frac{J}{hr\text{-}Pa\text{-}m^3}$ †	Bed Uniformity
UOP Proprietary	UOP 2	1522	343,900	3.0×10^6	Excellent
$Pt\text{-}Ir/Al_2O_3$	W. R. Grace	1256-1589	327,400	2.8×10^6	Ragged
Stab. Pt/Al_2O_3	Matthey Bishop	1611	348,000	5.2×10^6	Ragged
JM Proprietary	Johnson Matthey	1589	603,300	7.2×10^6*	Excellent
Co_2O_3/Al_2O_3	Pfefferle 3	1617	443,100	5.1×10^6*	Excellent
Co_2O_3/Zirconia Spinel	Acurex 3	1644	661,400	7.8×10^6*	Excellent
Noble Metal/ Proprietary	Acurex 4	1756	2,070,000	38.9×10^6*	Excellent

**All results with natural gas/methane fuel
*Bed not blown out
†Multiply entry by 2.7 for Btu/hr-atm-ft³

The first three catalysts, either precious metal or proprietary materials, exhibited volumetric heat release rates (q''') of approximately 3.7 x 10^6 J/hr-Pa-m^3 (10 x 10^6 Btu/hr-atm-ft^3) at blowout conditions. The next three, either proprietary or cobalt oxide catalysts, reached approximately 7.4 x 10^6 J/hr-Pa-m^3 (20 x 10^6 Btu/hr-atm-ft^3) without blowing out. This heat release rate represents the maximum facility capability in the screening test configuration. It is apparent that the cobalt oxide catalysts are generally capable of higher heat release rates than the precious metals in the graded cell configuration. The oxides required operation at higher temperature, however, to produce combustion efficiencies comparable to the precious metals at lower temperatures. The last catalyst, noble metal on a proprietary substrate, was tested to the limits of the test facility without blowing out.

During graded cell catalyst testing, operating temperatures were varied from 1367K to over 1978K (2000 to 3100°F). Thermal NO_x data were obtained with natural gas as the primary test fuel. A number of the test models are compared in Figure 2. From 1367 to 1644K (2000 to 2500°F), little variation among the NO_x emissions with catalyst type is apparent with NO levels below 20 ppm. At 1756 to 1867K (2700 to 2900°F), the NO_x production rate begins to increase, as with conventional flame combustion.

In Figure 2, two different catalyst geometries are shown for fuel-lean operation in the 1644 to 1978K (2500 to 3100°F) range. The upper curve is for a two-segment graded cell model (A-029) that acted primarily as a flame holder for downstream gas phase reactions. The lower curve represents data for a three-segment catalyst (A-030) where significantly increased combustion occurs on the surface of the catalyst bed. It is apparent that maximizing the amount of surface reaction occurring in a catalytic combustor minimizes the production of thermal NO_x. These results indicate the importance of the graded cell configuration, particularly for thermal NO_x control in high excess air gas turbine configurations.

In addition to baseline catalyst screening tests, selected catalysts were tested to characterize conversion of fuel-bound nitrogen to nitrogen oxides with catalytic combustion. Ammonia was added to natural gas to simulate fuels of varying nitrogen content. Exhaust gas analyses for NO_x by chemiluminescent analyzer and for ammonia (NH_3) and cyanide (HCN) by specific ion electrode were performed.

A nickel oxide/platinum catalyst was prepared at Acurex and tested over a range of stoichiometries from 55 to 200 percent theoretical air at a nominal bed temperature of 2400°F. Fuel dopant concentration ranged from 2500 to 10,000 ppmv NH_3 in the fuel. The results are shown in Figure 3 as the percentage of the incoming NH_3 converted to NH_3, HCN, and NO. The NH_3 conversion to NO increased from zero levels under very fuel-rich conditions to better than 90 percent on the fuel-lean side. NH_3 conversion to HCN showed the opposite trend — high under rich conditions and decreasing to zero on the lean side. Unconverted ammonia was highest below 70 percent theoretical air and remained at low levels under lean combustion.

The total of these three curves (dashed line and cross symbols) represents all assumed NO_x precursor species for the NiO/Pt catalytic combustor. A distinct minimum occurs between 70 and 80 percent theoretical air, where only 20 percent of the fuel nitrogen is converted to NO_x precursors.

A second graded cell catalyst (cobalt oxide/platinum) was tested with simulated fuel nitrogen. The fuel nitrogen conversion is shown in Figure 4. The ammonia conversion to nitric oxide provided the same characteristic curve as the nickel oxide/platinum catalyst. Differences in the HCN and NH_3 species measured, however, resulted in lower total NO_x precursor (NO + NH_3 + HCN) levels under fuel-rich conditions. The minimum occurred at a lower value of theoretical air (60 percent) than that of the previous nickel oxide catalyst (75 percent). The cobalt oxide catalyst could thus be operated fuel rich without dilution to achieve low conversion of fuel-bound nitrogen to nitrogen oxides.

The low fuel nitrogen conversion of these two catalysts at 60 to 80 percent theoretical air has important system implications. Combustors which could operate fuel-rich, possibly with staging, have potential for fuel NO_x control. This characteristic of the catalytic combustor under fuel-rich conditions is the basis for the two-stage catalytic combustor developed under this program.

Because of the significance of controlling fuel NO_x with catalytic combustors, additional testing of NH_3-doped propane and methane was conducted. It should be noted that fuel N conversion in rich catalytic combustion is achieved for much shorter residence times than those associated with conventional rich-lean combustion systems. Tests covering a range of stoichiometries from rich to lean were run to determine the effect of theoretical air, bed temperature, mass throughput, fuel type, and fuel-bound nitrogen type and concentration on the conversion of fuel-bound nitrogen to NO_x or NO_x precursors. In addition, an oxygen/argon mixture was used as the oxidant in a series of tests to perform a nitrogen balance across the catalytic combustor. Test results indicate that operating the combustor at lower bed temperatures (1367K compared to 1478K) minimizes the formation of fuel NO_x under lean conditions but does not affect the formation of NO_x precursors under rich conditions. Figure 5 shows the results for a proprietary UOP catalyst tested with ammonia-doped natural gas fuel. The lower bed temperature is postulated to minimize gas phase reactions, thereby minimizing NO_x formation under lean conditions. Under fuel-rich conditions, however, the stoichiometry has a much greater effect than bed operating temperature.

The effect of fuel nitrogen concentration on NO_x formation under lean conditions is shown in Figure 6. Using the proprietary UOP catalyst at 1478K bed temperature, the conversion of NH_3 to NO_x was seen to decrease as nitrogen weight percent in the fuel increased.

The results of nitrogen mass balance investigations using oxygen/argon as oxidizer instead of air are shown in Table III. As the table indicates, a maximum deviation of ±12 percent between the input fuel nitrogen content and the measured nitrogen species in the combustion products was obtained, except for two data points. N_2O was not detected for any test condition. Under fuel-rich conditions, as expected, N_2 was the dominant product of the chemically bound nitrogen conversion process.

Design criteria for the graded cell catalyst concept also included scaleup, pressure, and preheat characteristics. Catalyst blowout was again selected to compare activity. Based on the results of small-scale testing, a Universal Oil Products catalyst was selected for scaleup. Analytical modeling predicted that combustion throughput capability would scale proportionately to bed frontal area. Therefore, the bed diameter was increased to provide a 2.7 increase in frontal area over the small-scale model. Bed length remained fixed at 7.6 cm (3.0 inches).

Test data showed that maximum throughput (at blowout) did scale approximately with frontal area. Maximum throughput reported for the small-scale catalyst was 258.5 MJ/hr (245,000 Btu/hr) and 3.42×10^6 J/hr-Pa-m^3 (9.3×10^6 Btu/hr-atm-ft^3) volumetric heat release rate. This compares to a volumetric heat release of 4.38×10^6 J/hr-Pa-m^3 (11.9×10^6 Btu/hr-atm-ft^3) at 926.3 MJ/hr (878,000 Btu/hr) for the scaleup catalyst at 672K preheat.

A series of blowout tests were then conducted to determine the operational mass throughput limit of the catalyst for varying preheat and pressure conditions. The blowout points used are shown below.

BLOWOUT DATA -- CATALYST A-041

Data Point	Bed Temp		Preheat Temp		Max. Fuel Flowrate		Pressure	
	K	(°F)	K	(°F)	Kg/hr	(lbm/hr)	MPa	(atm)
1	1588	(2400)	608	(635)	15.0	(33.0)	.195	(1.93)
2	1588	(2400)	478	(400)	10.5	(23.1)	.140	(1.39)
3	1588	(2400)	389	(240)	8.4	(18.5)	.134	(1.33)
4	1588	(2400)	603	(625)	22.2	(49.0)	.301	(2.98)

Two things are evident from the data:

- Blowout scales linearly with pressure
  $(\dot{m}_{fuel\ max} = P_{atm} \times \dot{m}_{fuel\ max,\ 1\ atm})$
- Blowout for catalyst A-041 was exponential in preheat temperature, although a relatively weak exponential factor was determined.

Operation of the catalyst was, of course, possible at any combination of preheat and fuel flowrate below the blowout limits.

The exponential behavior of preheat temperature and its effect on blowout was shown in PROF-HET code predictions (Reference 2). The blowout data obtained support this prediction and can be employed as design criteria for operation of catalyst A-041 under varying conditions.

The graded cell catalyst screening tests identified the design criteria required for incorporating the graded cell configuration into system applications. Specifically, these criteria included mass throughput and heat release capabilities, emissions under varying operating conditions and with nitrogen-containing fuels, lightoff requirements, and current lifetime capabilities. In addition, the state of the art in catalyst development has been evaluated, including an understanding of preparation techniques, material capabilities, and material interactions.

SYSTEM CONCEPT TESTING

The design criteria generated for graded cell catalyst configurations were used in the specification of three small-scale systems incorporating heat extraction techniques. A radiative catalyst/watertube system exhibited a stoichiometric, water-cooled combustor for boiler application. A model gas turbine combustor utilized high excess air for catalyst and exhaust gas temperature control. Finally, a two-stage combustor was constructed to evaluate fuel nitrogen control with application to either boiler, furnace, or turbine equipment.

RADIATIVE CATALYST/WATERTUBE SYSTEM

The radiative catalyst/watertube concept is shown in Figure 7. A stoichiometric fuel/air mixture is fed to the radiative section which contains a close-packed array of catalyst elements and watertubes. The mixture is partially combusted by the catalyst which is kept at a low surface temperature by radiation heat loss to the watertubes. The combustion products and remaining unburned fuel and air are then passed to a downstream catalytic adiabatic combustor to complete combustion reactions. A final convective section extracts energy from the fully combusted gases. Both catalyst sections operate well below the maximum use temperature of the catalyst supports -- the radiative section by radiative cooling and the adiabatic section by dilution of the fuel/air mixture with exhaust products from the radiative section. The radiative section was constructed and tested independently of the downstream adiabatic combustor and convective sections.

An initial test series was conducted using a platinum catalyst on Coors alumina cylinders. Stoichiometry was varied from 50 to 219 percent theoretical air and fuel mass flowrate from 2.1 to 6.7 kg/hr (4.7 to 14.8 lbm/hr) of natural gas. Preheat conditions were also varied. Figure 8 shows the energy extracted by the cooling tubes out of the total available energy at the bed inlet as a function of stoichiometric ratio. The total available energy includes the fuel heating value and the sensible preheat energy. Thermal input to the catalyst cylinders is primarily controlled by the adiabatic flame temperature of the fuel/air mixture. This temperature peaks near unit stoichiometry, and as a consequence, the tube temperatures have a corresponding maximum. As theoretical air percentage increases above 100 percent, catalyst surface temperature begins to decrease, decreasing the radiant exchange to the watertubes. The higher total mass throughput, however, also increases convective heating of the watertubes such that at fixed fuel flowrate the energy exchange does not fall off rapidly. Overall combustion efficiency at 100 percent theoretical air was calculated as approximately 37 percent from the data. Significant emissions of CO and HC were measured for the radiative section due to the incomplete combustion. NO_x levels were consistently below 2 ppm as measured.

The radiative section was also tested to evaluate fuel nitrogen conversion characteristics of the system. For those tests, natural gas was doped with ammonia and stoichiometry was varied from 52 to 120 percent theoretical air.

Figure 9 shows the fuel nitrogen conversion characteristics of the radiative system for natural gas doped with 2000 ppm of ammonia. Low NO_x and high NH_3 values above 100 percent theoretical air are consistent with the incomplete combustion characteristics of the radiative section. The low point in the total NO_x precursor curve (NH_3 + HCN + NO_x) at 60 percent theoretical air is similar to those obtained for metal oxide graded cell catalysts. It should be noted that this low level of conversion is attained even though the fuel is not fully combusted.

The radiant section as tested is not fully suited for complete system development. The addition of the downstream adiabatic catalytic combustor would result in too high a temperature in that region at stoichiometric conditions. This occurs since combustion efficiency in the first stage was not quite as high as expected at the nominal 4.3 kg/hr (9.5 lbm/hr) design condition. The radiative catalyst/watertube section did exhibit excellent performance at stoichiometric conditions with very low levels of NO_x. The potential for control of fuel nitrogen conversion and the extremely stable operation experienced under all test conditions make it attractive for future boiler applications.

MODEL GAS TURBINE COMBUSTOR

Since the graded cell catalyst was demonstrated to have the low preheat, high heat release, and pressure capabilities required for gas turbine applications, a 1055.1 MJ/hr (10^6 Btu/hr) model turbine can and fuel injection system were constructed. The system and catalyst are shown in Figure 10. Testing was performed at Acurex and Pratt and Whitney Aircraft (West Palm Beach, Florida) facilities. Acurex and UOP catalysts were prepared on both duPont alumina and Corning zirconia spinel support materials of varying configurations.

The model gas turbine combustor was first tested at Acurex with propane at pressures between 0.101 and 0.354 MPa (1 and 3.5 atmospheres). A heat release rate of 263.8 MJ/hr (250,000 Btu/hr) at 1478K (2200°F) bed temperature was run as the nominal test condition. No significant emissions of NO_x or CO were obtained.

Pratt and Whitney test data were obtained with propane, No. 2 oil, and No. 2 oil with 0.5 weight percent nitrogen as fuels. Heat release rates to 844 MJ/hr (800,000 Btu/hr) were achieved with low NO_x emissions for both propane and No. 2 oil. Some difficulty was encountered with flashback and flameholding on the fuel nozzles when running No. 2 oil. High CO and unburned hydrocarbon emissions resulted from operating at the low bed temperatures (near the breakthrough limit) required to avoid flashback. Variations in pressure under lean conditions were not found to affect emission levels. Tests run with pyridine-doped No. 2 fuel oil, however, increased the NO_x emissions levels, representing percentage conversions of fuel nitrogen to NO_x of 100, 61, and 55 percent for test pressures of 0.303, 0.505, and 0.707 MPa, respectively. Subsequent inspection of the test hardware showed that low liquid fuel inlet velocities due to a fabrication error causing all liquid fuel to be introduced through the large diameter gaseous fuel injection ports were responsible for the flashback and flameholding.

A final test series was conducted at Acurex (after the test hardware had been reworked) with natural gas, natural gas doped with ammonia, and No. 2 oil. Pressures from 0.101 to 0.808 MPa (1 to 8 atm) with natural gas and 0.101 to 0.505 MPa (1 to 5 atm) with fuel oil were included. A decrease in ammonia converted to NO_x with pressure was observed. These results are consistent with those obtained at Pratt and Whitney with pyridine-doped No. 2 fuel oil. Maximum throughput for the catalyst at 0.303 MPa, 1244K (3 atm, 2100°F) pressure and bed temperature, and 561K (550°F) preheat temperature was also investigated. At space velocities near 200,000 per hour, the catalyst began to break through with increasing CO and unburned hydrocarbon emissions. Nitrogen oxide emissions remained at near zero levels throughout the test. Full blowout was not achieved as control of catalyst temperature during breakthrough produced difficulties in system control. The maximum heat release obtained was 615 MJ/hr (583,000 Btu/hr).

Final tests were conducted with diesel fuel to compare emissions with those from natural gas. An increased bed temperature was maintained for the oil tests to maintain uniform bed conditions and suppress soot formation. The NO_x levels were higher than for natural gas (15 ppm compared to 3 ppm) due primarily to the small amount of fuel nitrogen in diesel fuel.

The results of the model gas turbine testing demonstrated the application of the graded cell concept in a system similar to current turbine combustor designs. High mass flowrates were achieved in a relatively small volume combustor. Overall pressure drop for the combustor and fuel injector were measured at less than 1 percent at 0.303 MPa (3 atmospheres) test pressure.

TWO-STAGE COMBUSTOR

The two-stage catalytic combustor is attractive for two reasons. First, it allows control of bed temperatures to those compatible with the support material without large excess air requirements. Second, the first stage can be operated fuel-rich, which has been shown to be advantageous for reduced conversion of fuel nitrogen to nitrogen oxides. A two-stage combustor was designed and constructed to exhibit these concepts.

The two-stage combustor is shown schematically in Figure 11. A fuel-rich mixture is introduced into the primary stage which contains a graded cell catalyst bed. The fuel is partially combusted, and the released energy is removed by an interstage heat exchanger. Sufficient secondary air is then injected into the combustion products to complete combustion of the remaining fuel in the second stage. The full system combustor would also include a second heat exchanger to remove the combustion energy released in the second stage.

The two-stage combustor containing two cobalt oxide catalysts was tested with natural gas at 0.101 MPa and 0.202 MPa pressures (1 and 2 atmospheres). Lightoff and steady-state operation presented no unusual control problems. The combustor was tested at an overall stoichiometry varying from 70 to 150 percent theoretical air at a nominal fuel flowrate equivalent to 211 MJ/hr (200,000 Btu/hr) heat release rate. The first stage stoichiometry was varied from 40 to 70 percent theoretical air. Ammonia was added to the natural gas fuel at a rate of 0.2 to 0.4 weight percent.

Bed temperatures ranged from 1256K to 1660K depending on theoretical air, for a relatively constant preheat of 617K (650°F). The energy extracted in the interstage heat exchanger represents 50 to 60 percent of the combustion energy generated in the first stage.

The results of the fuel nitrogen conversion data are shown in Figure 12 as a function of overall combustor stoichiometry. The data show that when operating above 100 percent theoretical air, only nitrogen oxides are normally present. Under overall fuel-rich conditions, fractions of ammonia and cyanide are also present. These results are consistent with fuel nitrogen data obtained on the single cobalt oxide catalyst (model A-037, Figure 4). The data in Figure 12 show a nominal 30 percent conversion rate of fuel nitrogen to NO_x precursors with a value of approximately 27 percent near overall stoichiometric conditions. A slight decrease in conversion was noted at 0.202 MPa (2 atm) pressure.

The data shown in Figure 12 at approximately 10 percent conversion levels varied in test conditions from the other data in two respects:

1. Most significantly, the first stage was operated at higher values of theoretical air (60 and 70 percent) compared with 50 percent for the initial data, and
2. The first stage catalyst had experienced some sooting by later test times when the data were taken, causing the catalyst to operate at lower temperatures with incomplete combustion.

The first stage sooting of the cobalt catalyst proved to be a limiting factor in the test life of the system. The incomplete combustion occurring at later test times was evident by increasing measured carbon monoxide levels.

The demonstration of the two-stage combustor showed a number of important results:

1. The two-stage combustor is effective in controlling conversion of fuel nitrogen to nitrogen oxides under stoichiometric and fuel-lean conditions.
2. A slight decrease in nitrogen conversion was found at 0.202 MPa (2 atmospheres) pressure.
3. The variation of first stage stoichiometry impacts overall fuel nitrogen conversion.
4. First stage sooting of the cobalt oxide catalyst was a limiting factor in combustor operating life.

Application of the concept of both boiler and turbine systems is possible. Convective heat exchangers downstream of each catalyst stage would provide for steam raising in boiler applications. Interstage cooling would not be required for gas turbine systems where high excess air in the second stage could be used to control the catalyst and exhaust gas temperatures. Further work is required for optimization of the system and catalyst elements for specific applications.

CONCLUSIONS

As a result of this research and development program, significant progress has been made toward developing a practical catalytic combustion system. Before the step to demonstration can be taken, however, additional work relating to the integration of the catalytic combustor into the total combustion system must be performed.

Based upon the analysis and test results of this program, the design, fabrication, and operation of catalytic combustors with high volumetric heat release rates and low emissions have been demonstrated. Both precious metal and oxide catalysts have been tested over a wide operating temperature range. The precious metal catalysts should be limited to temperatures below 1589K (2400°F) for catalyst life considerations, while oxide catalysts can be operated for long periods at temperatures above 1644K (2500°F). Catalyst performance has been greatly enhanced through the use of graded cell monoliths and higher catalyst loadings.

Catalytic combustors have been shown to be effective in controlling both thermal and fuel NO_x emissions. The thermal NO_x control appears to result from maximizing surface reactions in the combustor, while fuel NO_x can be minimized by operating at a rich fuel/air ratio which minimizes the formation of NH_3, HCN, and NO, with complete combustion of CO and HC at a later time.

The maximum throughput of a catalytic combustor is a linear function of pressure and an exponential function of preheat. Thus, for a given preheat, the catalyst is face velocity limited in throughput ability.

Small-scale catalytic combustion system configurations have been tested and show the feasibility of direct radiative removal of bed heat for temperature control, two-stage catalytic combustion for temperature and fuel NO_x control, simulated exhaust gas recirculation through the use of nitrogen diluent for temperature control, and high excess air operation. The combustion system concepts that have been operated show that it is possible to operate near stoichiometric conditions with less than 10 ppm NO_x and CO in a natural gas-fired catalytic combustor.

A number of areas in catalytic combustion need to be addressed to capitalize on the progress to date. Additional testing of simple and mixed oxide catalysts for combustion and fuel nitrogen conversion abilities is needed, along with life testing of selected catalysts to 1000 hours at various pressures.

Exploratory work with heavy fuel oils (Nos. 4, 5, and 6) and pulverized coal should be conducted to determine system feasibility and fuel preparation problems. The potential of catalytic combustion in controlling NO_x emissions from the combustion of these fuels is great and needs early experimental verification.

Development of auxiliary systems required to interface with the catalytic combustor is also needed. This includes lightoff systems, temperature control systems, and fuel and air introduction systems. In addition, further testing of the radiative catalyst/watertube, two-stage combustor, and gas turbine combustor systems is needed to more thoroughly define operating ranges with a variety of fuels.

Finally, the design, fabrication, and operation of a demonstration unit should be undertaken when the above work is completed. The demonstration unit would be operated as a laboratory device for several months prior to the initiation of field demonstration tests.

REFERENCES

1. Kesselring, J. P., et al., "Design Criteria for Stationary Source Catalytic Combustors," published in Proceedings of the Second Stationary Source Combustion Symposium, Volume III, EPA-600/7-77-073c, July 1977, pp. 193-228.

2. Kelly, J. T., et al., "Development and Application of the PROF-HET Catalytic Combustor Code," Paper No. 77-33 presented at the Western States Section of the Combustion Institute, October 1977.

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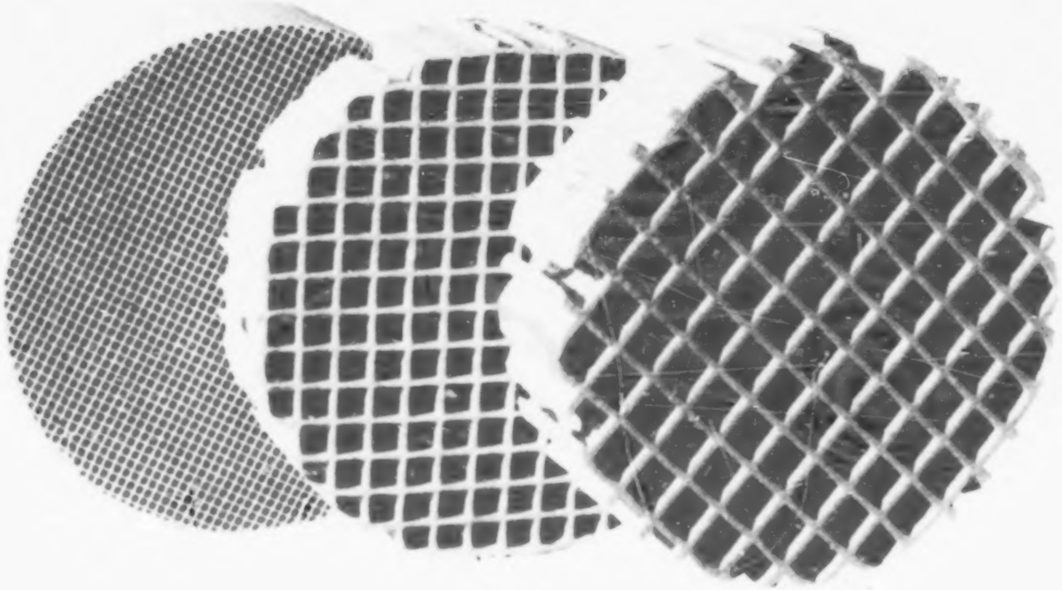

Figure 1. Corning square-celled extruded monolith structures.

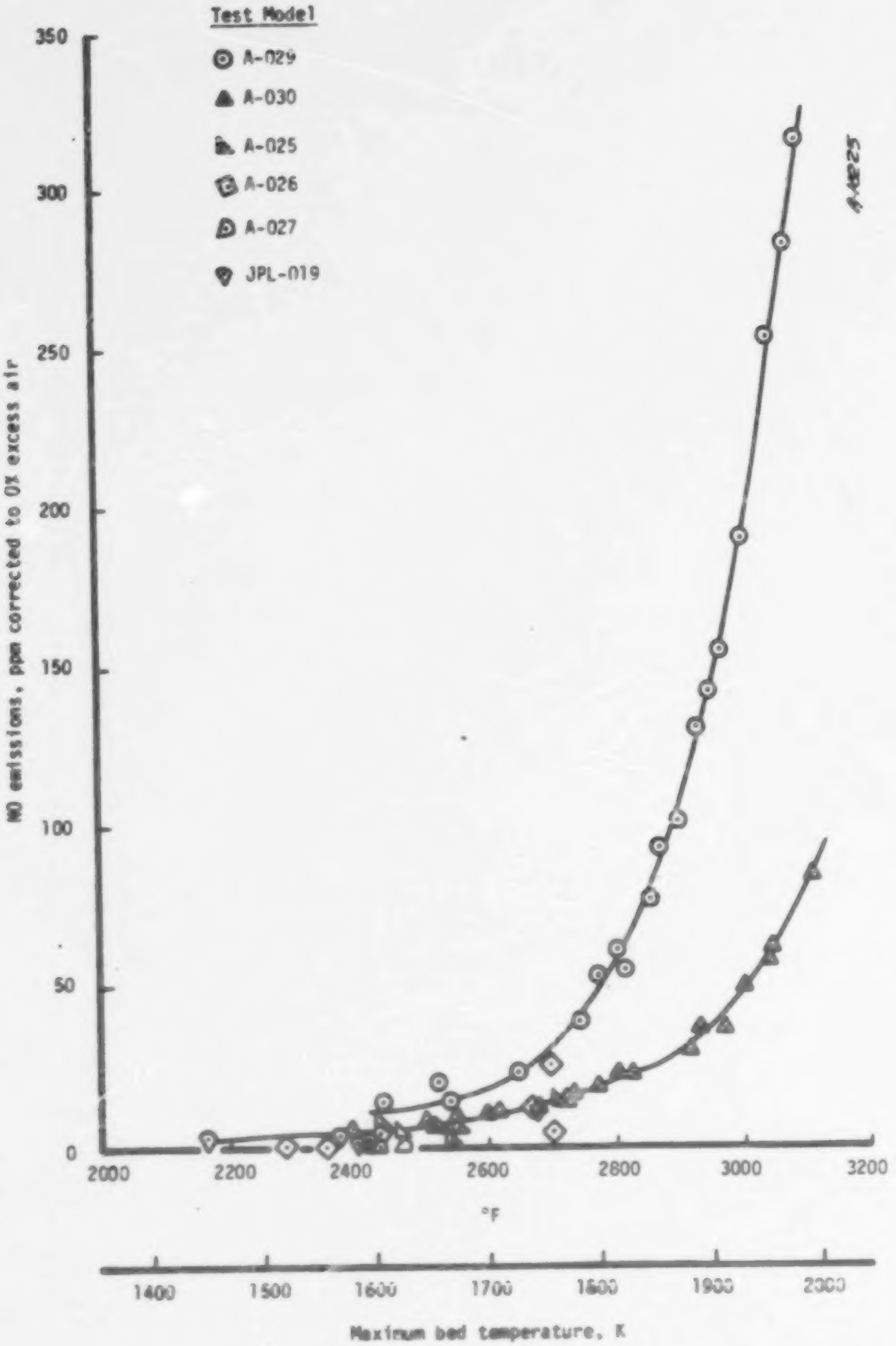

Figure 2. NO_x comparison corrected to 0-percent excess air.

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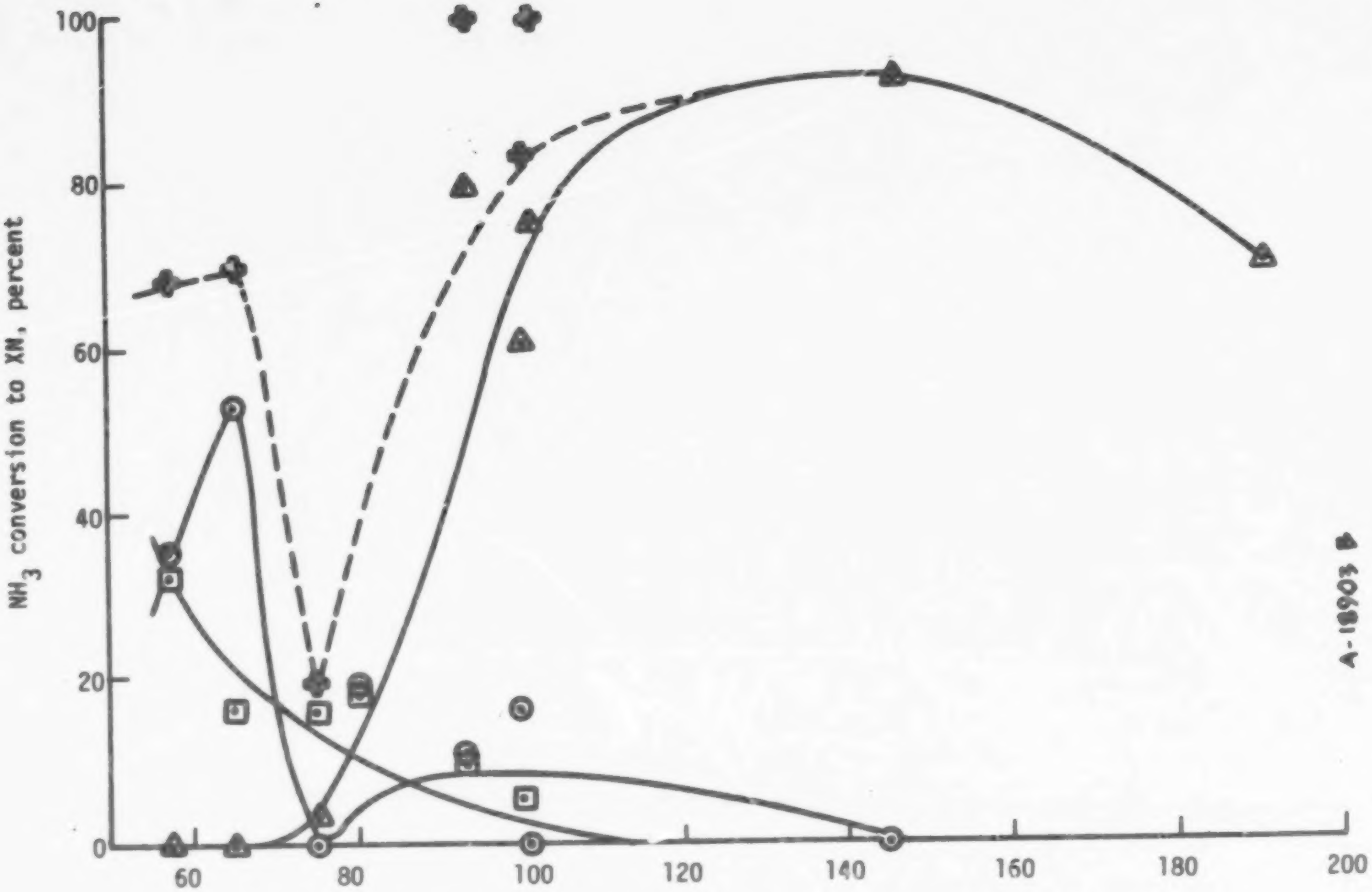


Figure 3. Theoretical air, percent.

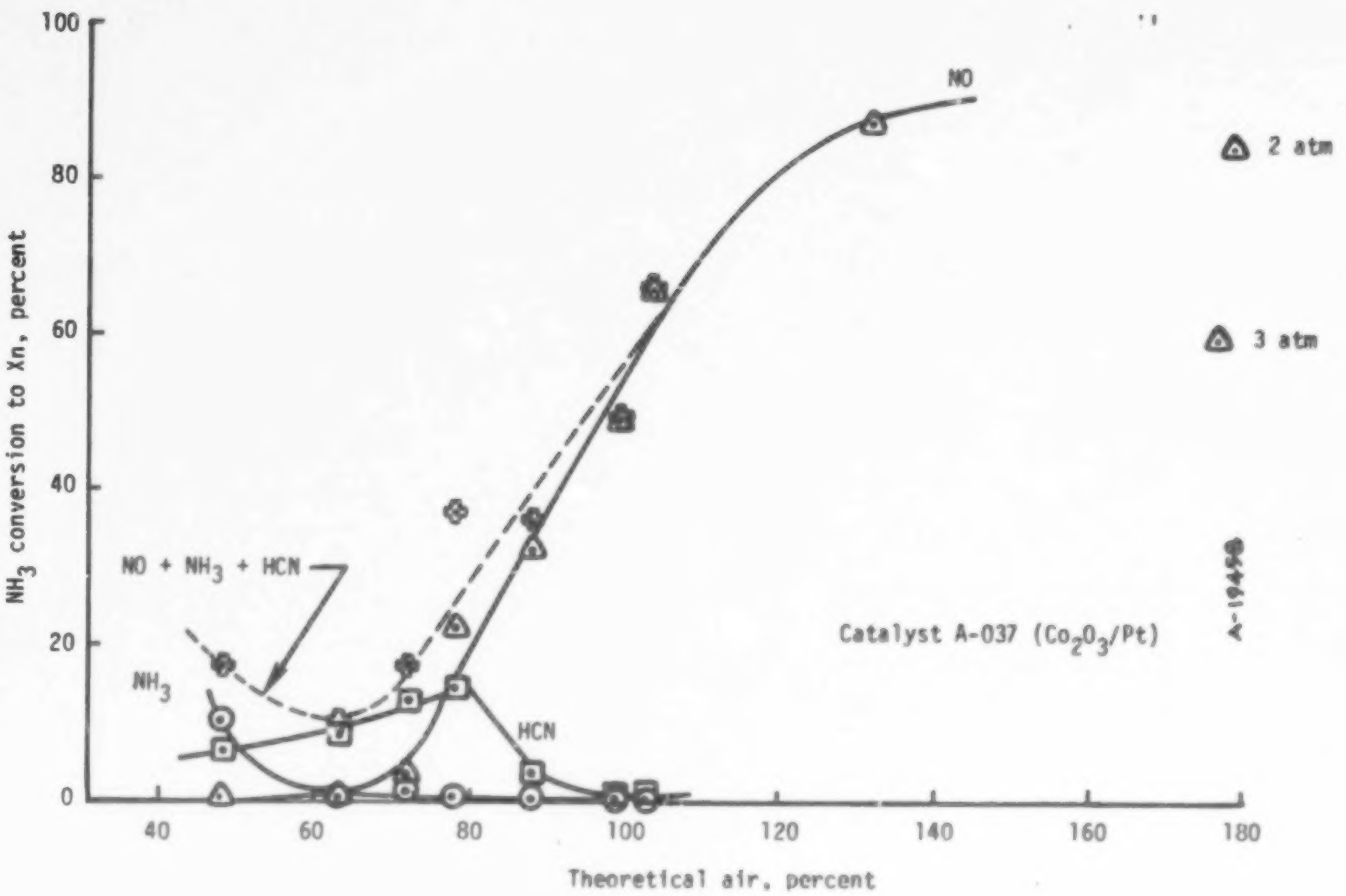


Figure 4. NH3 conversion characteristics, natural gas doped with ammonia Co_2O_3/Pt catalyst.

UOP catalyst
Natural gas fuel
Nitrogen concentration = 0.5 wt percent
Fuel flowrate = 25.3 MJ/hr (24,000 Btu/hr)

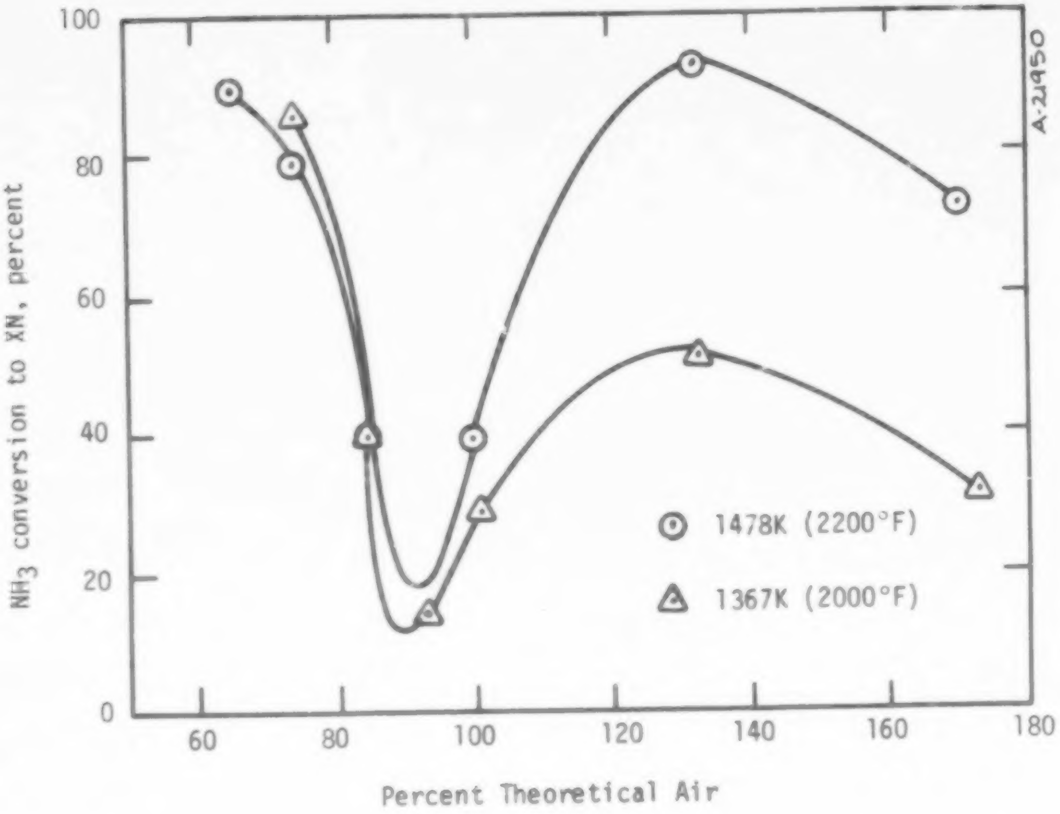
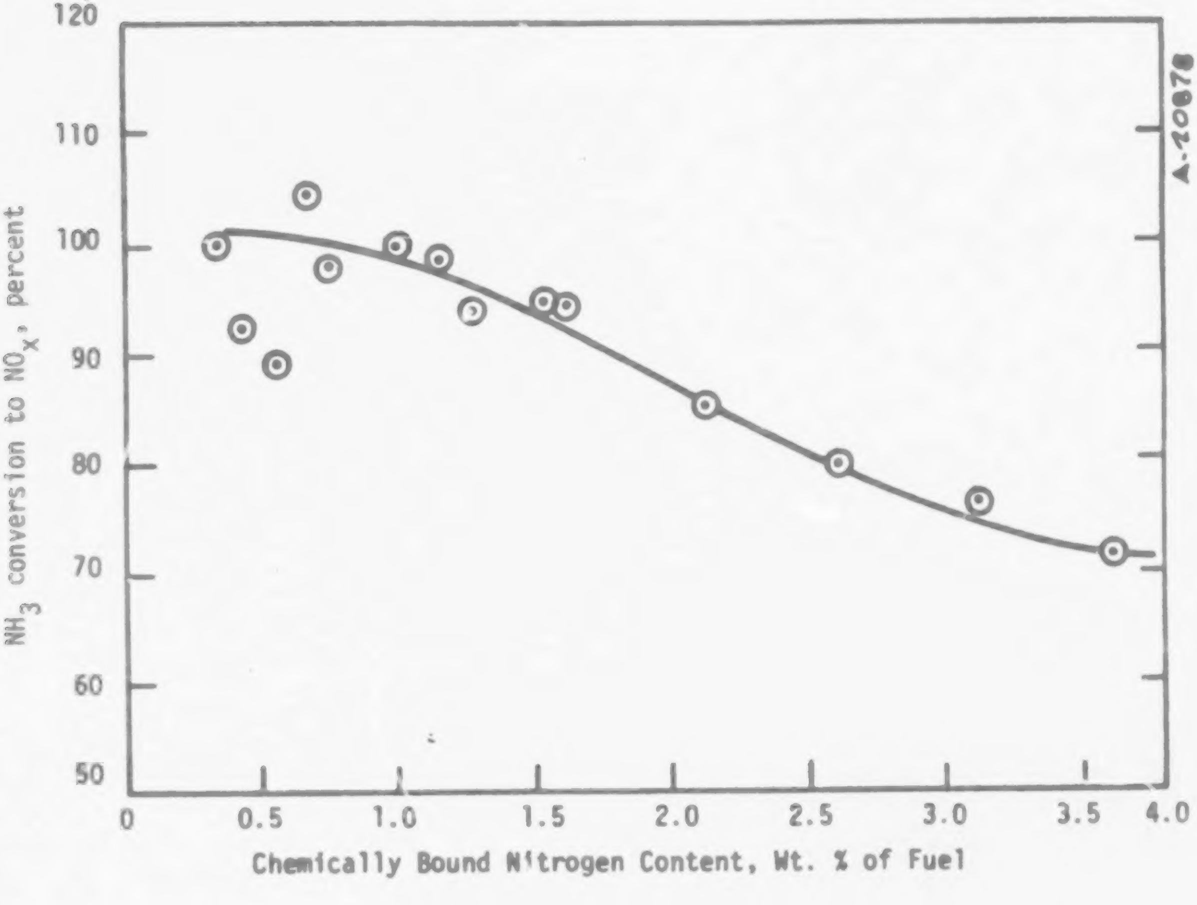


Figure 5. Effect of bed temperature on NH_3 conversion to NH_3+HCN+NO_x, UOP catalyst.



UOP Catalyst
Propane Fuel
Theoretical Air = 310 percent
Fuel flowrate = 25.3 MJ/hr (24,000 Btu/hr)
Bed Temp. = 1478K (2200°F)

Figure 6. Effect of nitrogen content on NH_3 conversion to NO_x, UOP catalyst.

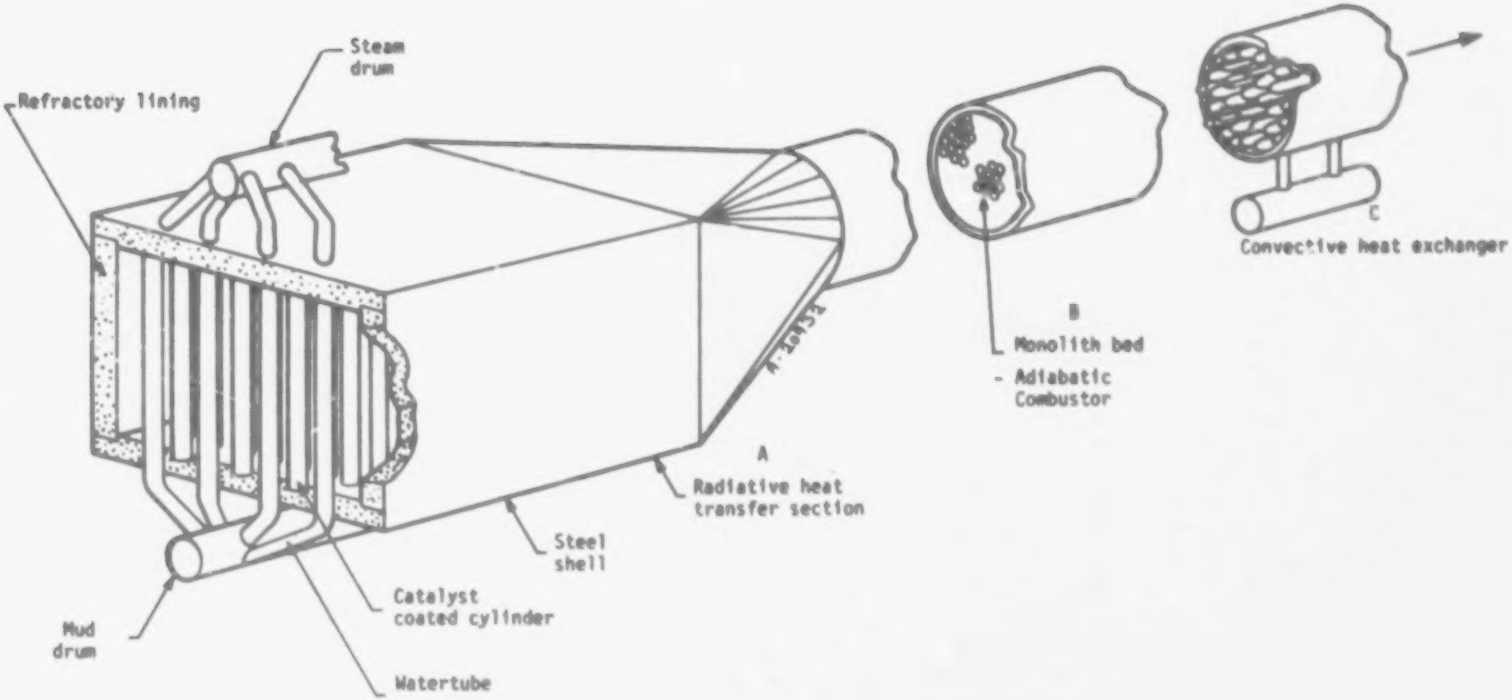

Steam drum
Refractory lining
B
Monolith bed
- Adiabatic Combustor
C
Convective heat exchanger
A
Radiative heat transfer section
Steel shell
Catalyst coated cylinder
Mud drum
Watertube

Figure 7. Radiative watertube boiler concept.

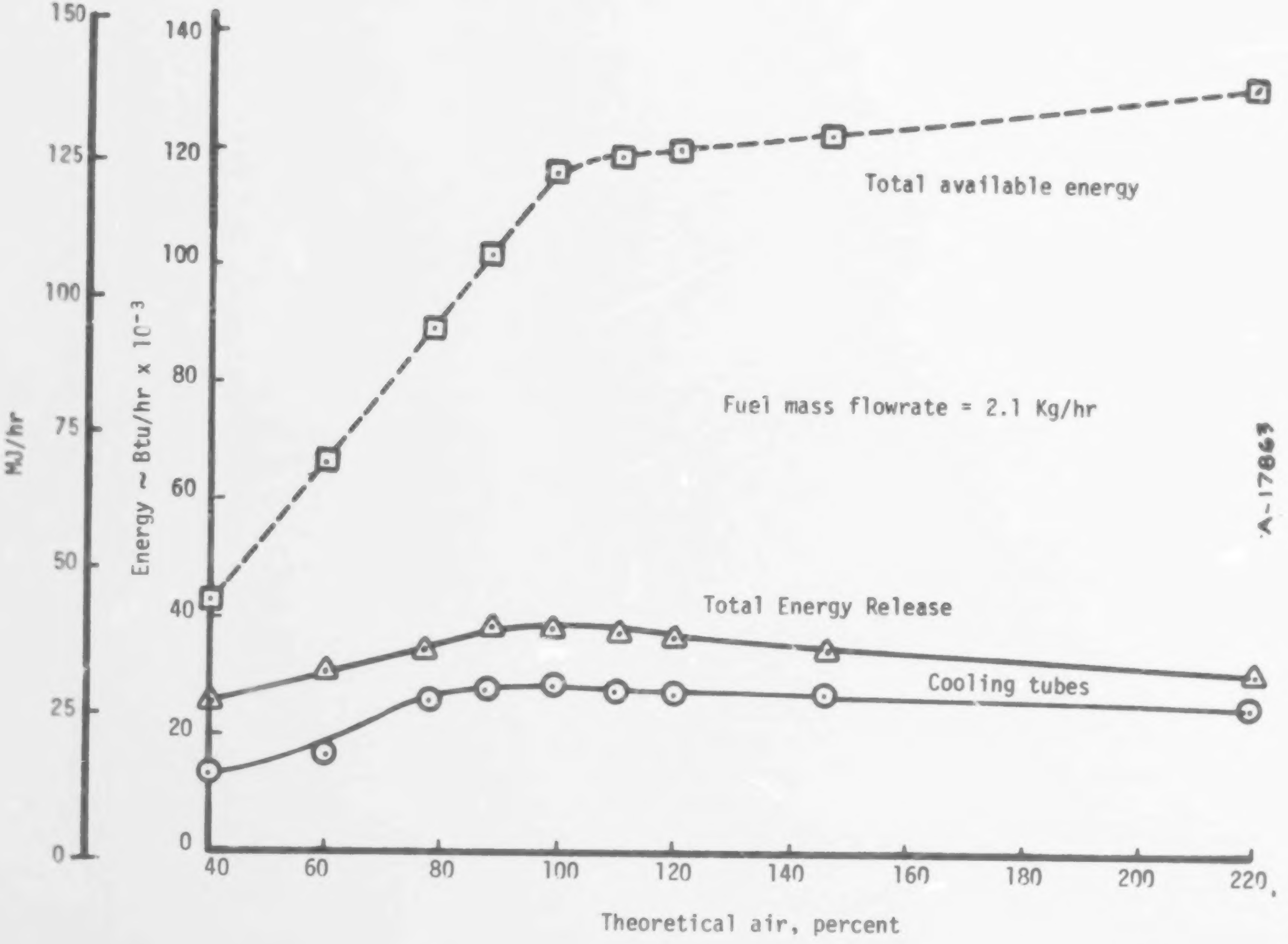


Figure 8. Radiative catalyst/watertube system energy release vs theoretical air.

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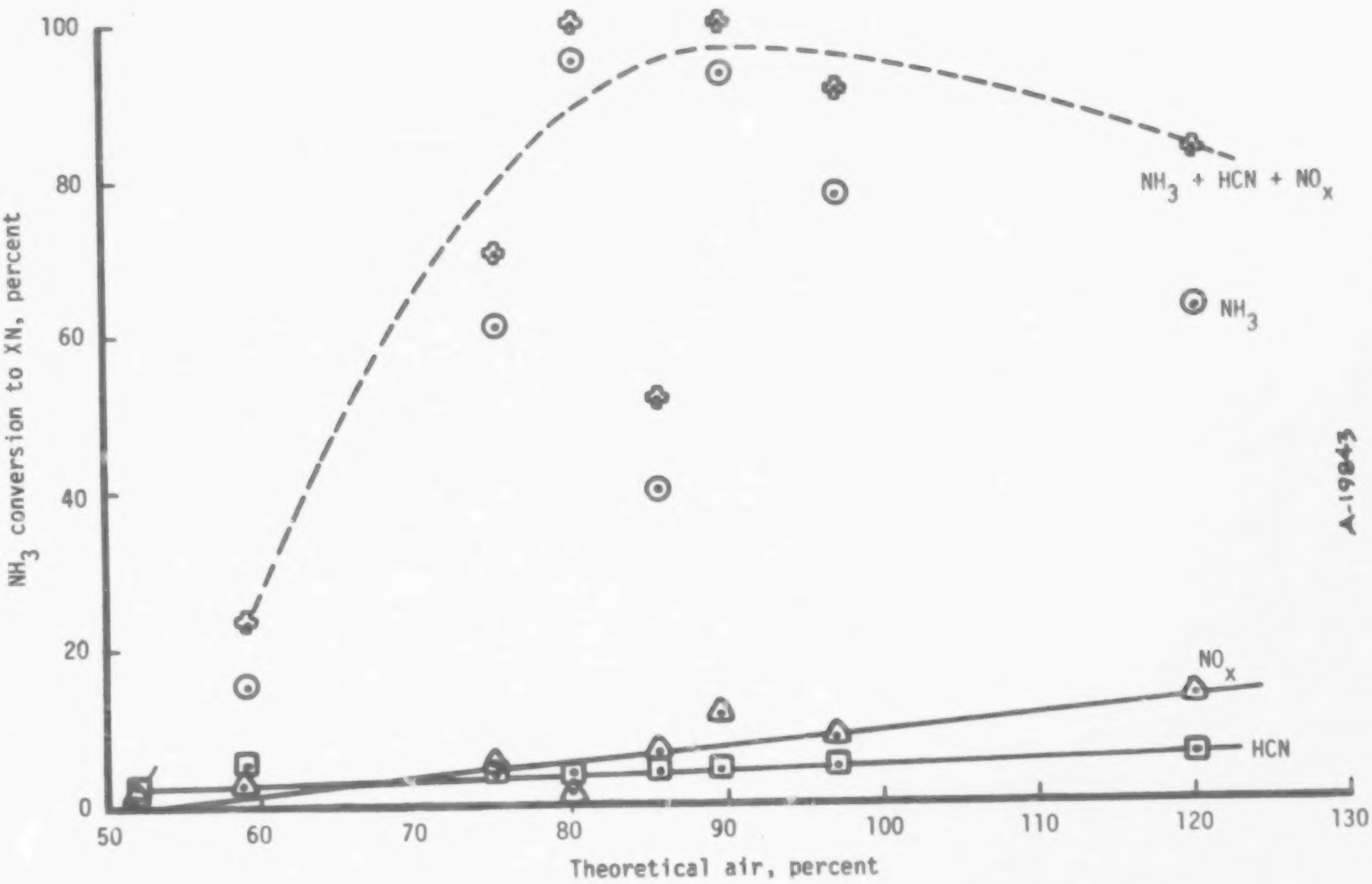

Figure 9. Radiative catalyst/watertube system, fuel nitrogen conversion

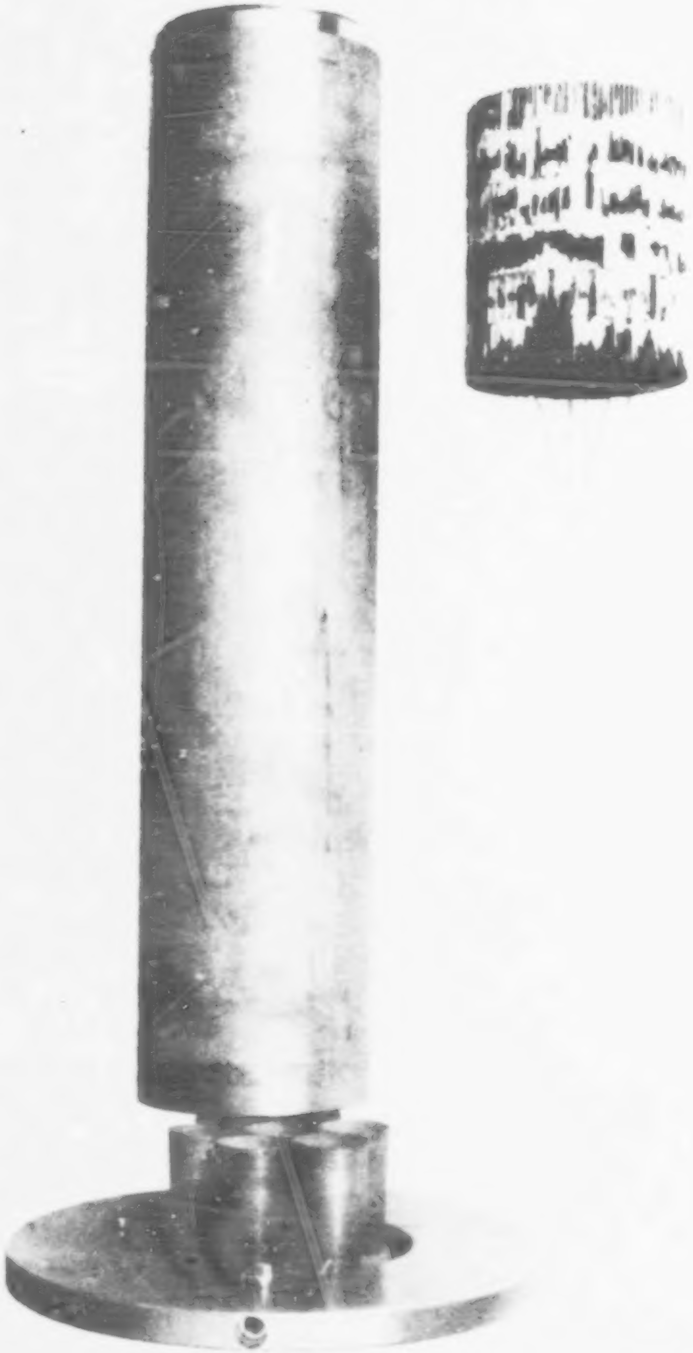

Figure 10. Model gas turbine combustor.

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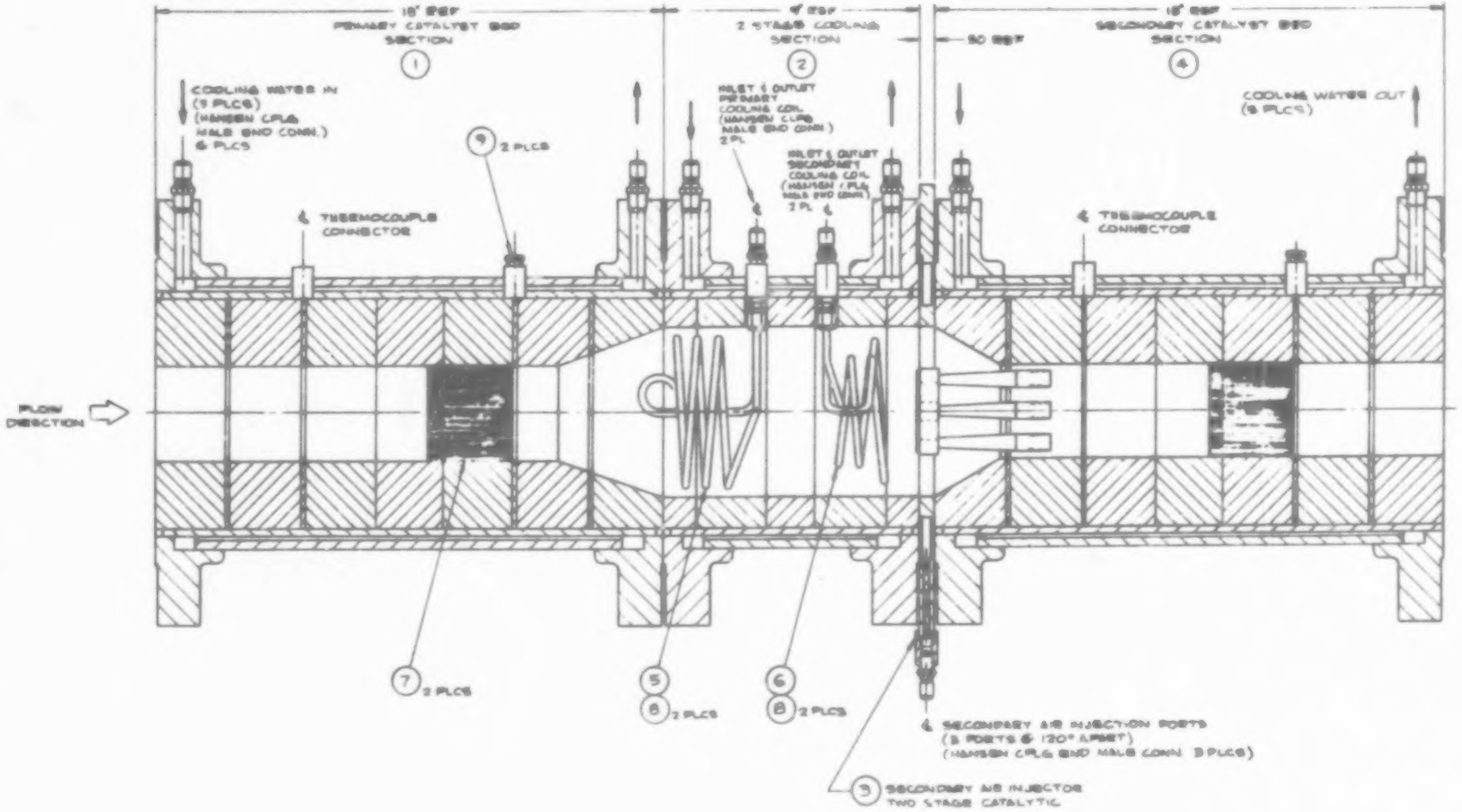
18" REF
PRIMARY CATALYST BED SECTION
①
4" REF
2 STAGE COOLING SECTION
②
.50 REF
18" REF
SECONDARY CATALYST BED SECTION
④
COOLING WATER IN (3 PLCS) (HANSEN CPLG MALE END CONN.) 6 PLCS
⑨ 2 PLCS
INLET & OUTLET PRIMARY COOLING COIL (HANSEN CLPG MALE END CONN.) 2 PL
INLET & OUTLET SECONDARY COOLING COIL (HANSEN CPLG MALE END CONN.) 2 PL ℄
℄ THERMOCOUPLE CONNECTOR
℄ THERMOCOUPLE CONNECTOR
COOLING WATER OUT (3 PLCS)
FLOW DIRECTION
⑦ 2 PLCS
⑤
⑧ 2 PLCS
⑥
⑧ 2 PLCS
℄ SECONDARY AIR INJECTION PORTS (3 PORTS @ 120° APART) (HANSEN CPLG END MALE CONN 3 PLCS)
③ SECONDARY AIR INJECTOR TWO STAGE CATALYTIC

Figure 11. Two stage catalytic arrangement.

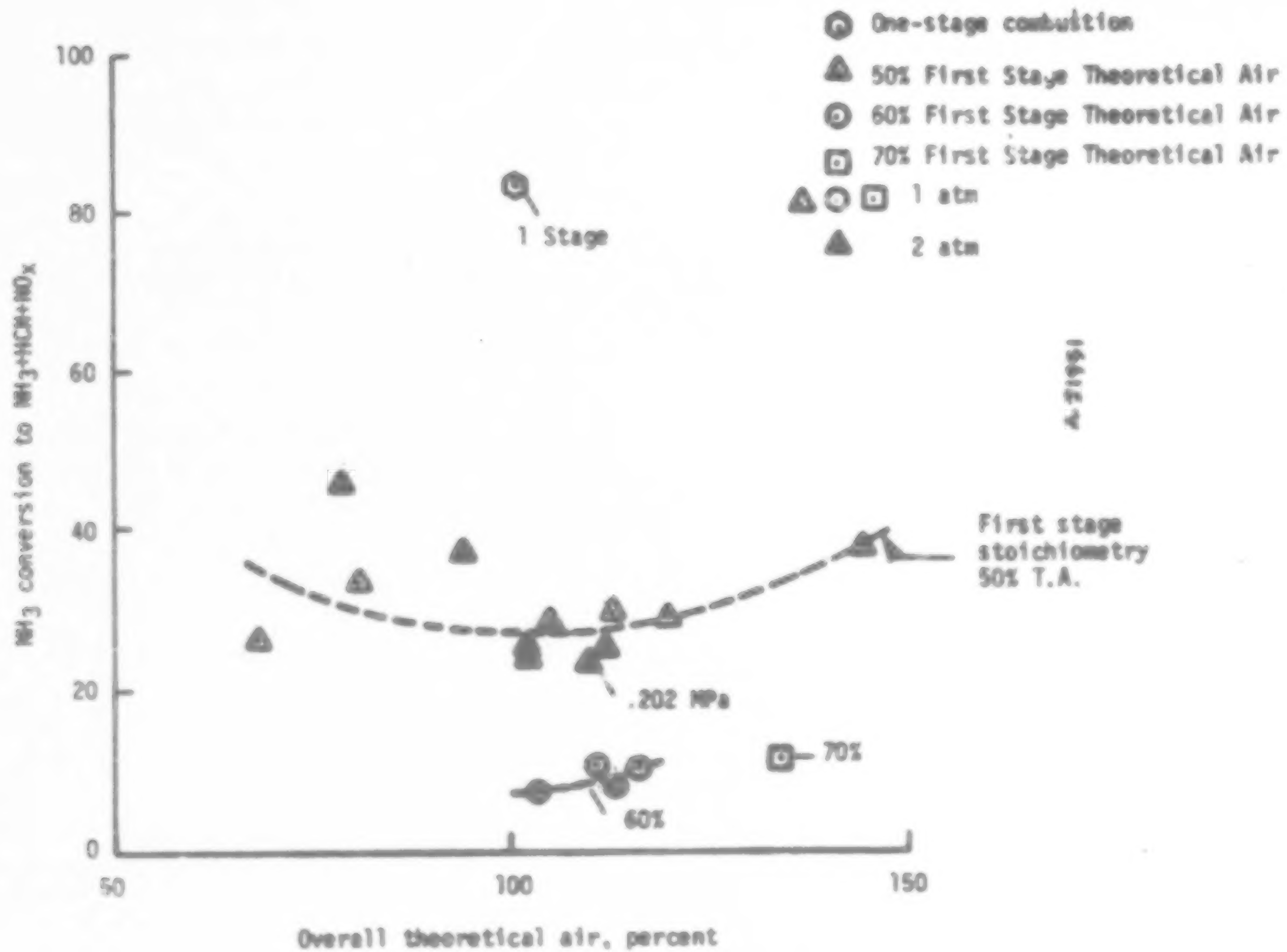

Figure 12. Two-stage combustor fuel nitrogen conversion.

TABLE I. GRADED CELL CATALYST MODELS

Sample No.	No. of TC	Substrate Manu.	Substrate Type	Washcoat Manu.	Washcoat Type	Catalyst Manu.	Catalyst Type	Wt. %	Gms	Dates Tested	Fuel	Test Purpose
AERO-025	5	DuPont	Alumina	[illegible]	Rare earth stabilized alumina 10-18 Wt. %	Grace	Pt/Ir	0.6-1.0	.47/.76/.80	4/25 – 4/29/77	Nat. Gas	Screen Grace Pt/Ir catalyst
AERO-026	6	DuPont	Alumina	UOP	Proprietary	UOP	Proprietary	–	–	6/20 – 6/29/77	Nat. Gas	Screen UOP catalyst
AERO-027	6	DuPont	Thoria impregnated alumina	None	–	W. Pfefferle	Pt/Ir/Os	0.29	.30/.24/.17	6/30 – 7/1/77	Nat. Gas	Determine effects of high melting point precious metals and catalyst without washcoat
AERO-028	–	DuPont	Zirconia impregnated alumina	None	–	W. Pfefferle	Pt/Ir/Os	0.29	.52/.08/.09	–	–	Not to be tested based on results of A-027.
AERO-029	6	Corning	Zirconia spinel	None	–	W. Pfefferle	RIO/Pt	0.29-0 Pt .29/.48/ 2.9 RIO	0.0/.31/0 .5/.8/5.0	7/10 – 7/11/77	Nat. Gas	Investigate metal oxide catalyst capabilities (no washcoat). Perform high temp. operation ([illegible]°F).
AERO-030	6	Corning	Zirconia spinel	None	–	Aero	Co_3O_4/Pt	2.4-0 Pt 5.4-7.8 Co_3O_4	4.1/0/0	7/14 – 7/21/77	Nat. Gas	Metal oxide comparison, extensive evaluation
AERO-031	6	DuPont	Alumina	Matthey Bishop	Proprietary	Matthey Bishop A	Stab. Pt	.33-.76	–	8/2 – 8/10/77	Nat. Gas	Compare to A-032
AERO-032	6	DuPont	Alumina	Matthey Bishop	Proprietary	Matthey Bishop B	Stab. Pt	.88-1.58	–	7/28 – 7/29/77	Nat. Gas	Screen Matthey Bishop catalyst
AERO-033	7	Corning	Zirconia spinel	None	–	Aero	RIO/Pt-Pd	.87-0 Pt 2.2/.98/ 7.0 RIO	15/0.7/0 Pt 5.0/2.1/ 4.5 RIO	9/14 – 9/20/77	Nat. Gas	Fuel nitrogen and pressure testing } Test difficulties precluded data results
AERO-034	7	Corning	Zirconia spinel	Oxy-Catalyst	γ-Alumina 4 Wt. %	Aero	Co_3O_4/Pt	2.2-0 Pt 9.3/5.6/ 4.3 Co_3O_4	3.0/0/0 Pt 7.7/9.9/ 20.0 Co_3O_4	9/22 – 9/27/77	Nat. Gas	Comparison to A-033 }
AERO-035	7	DuPont	Alumina	Matthey Bishop	Proprietary	Matthey Bishop C	Stab. Pt	1.98/1.2/ 0.9	–	10/[illegible] – 10/6/77	Nat. Gas	Screening comparison
AERO-036	7	Corning	Zirconia spinel	Aero	Zirconia Magnesia .8-1.0 Wt. %	Aero	RIO/Pt	1.8/2.1/ 2.1 RIO 1.2/0.9/ 0 Pt	3.6/3.2/ 4.0 RIO 2.0/1.4/ 0 Pt	10/10 – 10/12/77	Nat. Gas	Fuel nitrogen testing
AERO-037	4	Corning	Zirconia spinel	None	–	Aero	Co_xO_y/Pt	2.7/2.8/ 3.4 Co_xO_y 4.0/0/0 Pt	4.3/4.9/ 10.1 Co_xO_y 6.7/0/0 Pt	12/5 – 12/23/77	Nat. Gas & Methane	Fuel nitrogen and pressure testing
AERO-038	5	DuPont	Alumina	None	–	W. Pfefferle	Co_3O_4	10.0/1.1/3.0	10.3/2.9/0.0	12/28 – 12/29/77	Nat. Gas	Investigate catalyst-support interactions
AERO-040	5	DuPont	Alumina	Johnson Matthey	Proprietary	Johnson Matthey	Proprietary	–	–	1/25 – 2/6/78	Nat. Gas	Screen Johnson Matthey catalyst
AERO-041	4	DuPont	Alumina	UOP	Proprietary	UOP	Proprietary	–	–	12/30/77 – 1/3/78	Nat. Gas	Catalyst scaleup, 6.00-inch diameter

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TABLE II. SURFACE AREA AND DISPERSION MEASUREMENTS ON GRADED CELL CATALYSTS

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Sample No.	Surface Area m^2/g		Dispersion %		Catalyst	SEM/EDAX Results and Comments
	Pretest	Post-test	Pretest	Post-test		
AERO-025	1.55-2.49	0	1.5-4.9	0	Pt/Ir	No Pt or Ir found on back two segments by SEM/EDAX
AERO-026	5.94	0	–	–	Proprietary	
AERO-027	0.44	–	20.64	–	Pt/Ir/Os	
AERO-028	0.06	–	8.33	–	Pt/Ir/Os	Not combustion tested
AERO-029	0.60	0	–	–	NiO/Pt	
AERO-030	0.15	.01	–	–	Co_2O_3/Pt	
AERO-031	24.38	0	36.16	0	Stab. Pt	
AERO-032	11.99	0	9.11	0.20	Stab. Pt	
AERO-033	–	–	–	–	NiO/Pt-Pd	Invalid test data
AERO-034	–	--	–	–	Co_2O_3/Pt	Invalid test data
AERO-035	5.17	0.09	4.09	0	Stab. Pt	
AERO-036	–	–	–	–	NiO/Pt	
AERO-037	–	–	–	–	Co_2O_3/Pt	Zero surface area on each segment
AERO-038	0	–	–	–	Co_2O_3	
AERO-040	4.00	0	–	--	Proprietary	
AERO-041	6.37	0.50	–	–	Proprietary	

TABLE III. FUEL NITROGEN BALANCE

Run No.	Catalyst Type	Fuel-N Content (Wt. % of Fuel)	Theoretical Air (%)	Percent Conversion of Nitrogenous Species in the Combustion Products					Error (%)
				NO_x	N_2	NH_3	HCN	N_2O	
1	Pt	2.0	98	76.00	15.97	8.12	1.22	0	0.10
2	Pt		77	0.83	79.05	18.07	1.51		-0.56
3	NiO/Pt		200	80.57	13.19	1.81	1.21		-3.21
4	NiO/Pt		75	9.63	58.94	41.20	3.09		12.86
5	UOP	3.0	100	34.13	71.54	4.77	1.52		11.97
6			90	1.06	58.93	44.11	2.96		6.81
7			80	0.58	79.29	25.17	2.03		7.07
8			75	0.29	98.68	4.49	2.59		6.05
9			70	1.00	74.86	4.29	2.95		-16.91
10		2.4	100	23.77	68.20	5.90	0.72		-1.43
11		2.0	75	0.25	74.01	5.36	2.33		-18.02
12		3.6	90	0.68	61.50	42.34	4.71		9.23
13		3.0	80	3.28	54.68	37.92	16.79		12.66
14		3.0	70	2.47	45.60	41.91	7.00		-3.02

SESSION III: SPECIAL TOPICS

BY

Joshua. S. Bowen

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EPRI LOW COMBUSTION NO_X RESEARCH

BY

D. P. Teixeira
Electric Power Research Institute
Palo Alto, California

EPRI Low Combustion NO_x Research

by
D.P. Teixeira
Electric Power Research Institute

ABSTRACT

Recent results of EPRI's research and development efforts on the primary combustion furnace (PCF) concept to achieve low NO_x with pulverized coal will be presented. Principal of operation and earlier 4 million Btu/hr data will be reviewed. Recent data from nominal 50 million Btu/hr scale tests will be covered.

Full scale application issues related to the PCF will be discussed. A technical and economic comparison of combustion and post combustion control technologies will be made.

FLUE GAS TREATMENT TECHNOLOGY FOR NO_X CONTROL

By:

J. David Mobley
Process Technology Branch
Utilities & Industrial Power Division
Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

ABSTRACT

The Environmental Protection Agency has maintained a program to further the advancement of NO_x control by flue gas treatment technology since the early 1970's. The program consists of technology assessment and control strategy studies in conjunction with small scale experimental projects. These activities have shown that 90% reduction of NO_x emissions by selective catalytic reduction with ammonia has been commercially demonstrated on gas- and oil-fired sources in Japan, and that such processes are ready for test application on coal-fired sources. Based on the experience in Japan, successful application of the technology in the U.S. can be expected. Further, recent assessments indicate that 90% control of both NO_x and SO_x emissions by dry simultaneous control techniques warrants further investigation. However, wet simultaneous NO_x/SO_x removal processes are not currently attractive. The paper also assesses the need for highly efficient NO_x control in the U.S. and suggests that, although the nationwide need for flue gas treatment technology has not been established, certain regions will probably require application of the technology in the future.

INTRODUCTION

Nitrogen oxides (NO_x) and sulfur oxides (SO_x) in the atmosphere have been determined to have adverse effects on human health and welfare. To aid in preventing these adverse effects, the Industrial Environmental Research Laboratory at Research Triangle Park, N. C. (IERL-RTP) is leading the U.S. Environmental Protection Agency's (EPA's) efforts to develop and demonstrate NO_x and SO_x control technologies for stationary combustion sources.

Flue gas desulfurization technology has progressed to commerical application and has achieved 90% control of SO_2. Although NO_x control by combustion modification technology has been applied commercially, NO_x control by flue gas treatment technology has not been utilized in the U.S. Combustion modification technology reduces NO_x emissions by approximately 50% in a relatively cost effective manner. Flue gas treatment technology should be able to reduce NO_x emissions by 90% and has the potential for 90% control of both NO_x and SO_x emissions. The focus of this paper will be on flue gas treatment technology.

EPA is proceeding with small scale NO_x and NO_x/SO_x flue gas treatment experimental projects in parallel with technology assessment and control strategy studies. To save both development time and money, EPA is investigating Japanese technology for potential application to the U.S. coal-fired situation. Through these actions, the basic foundation will be established if the technology is required in the U.S. and acceleration of the development program becomes necessary.

This paper presents a summary of the past, current, and planned NO_x flue gas treatment programs of EPA and an overview of the technology in Japan.

EPA'S NO_X FLUE GAS TREATMENT PROGRAM

The thrust of EPA's current NO_x flue gas treatment (FGT) program is technology assessment and control strategy studies in conjunction with small scale experimental projects. The technology assessment and control strategy studies are mainly paper studies which examine various aspects of NO_x and NO_x/SO_x control technology, estimate if and when highly efficient NO_x control will be needed in the U.S., and assist in determining the appropriate scale of the experimental projects.

This paper will begin with a discussion of the following technology assessment studies:

- Assessment of Technology in Japan
- Assessment of Technology for U.S. Application
- Assessment of Technology for an Industrial Boiler New Source Performance Standard

Results of the control strategy assessment studies will then be presented:

- Assessment of Point Source Impact on Ambient NO_x Levels
- Assessment of the Need for NO_x Flue Gas Treatment Processes

Subsequently, experimental projects will be discussed:

- Hitachi Zosen NO_x Pilot Plant
- UOP-Shell NO_x/SO_x Pilot Plant

Finally, conclusions that can be drawn from these activities will be identified.

TECHNOLOGY ASSESSMENT STUDIES

Technology assessment studies report the rapid advances of the technology worldwide. These studies, which have concentrated on Japanese technology, evaluate the various processes and process features for interested parties in the United States. In addition, the feasibility of application of the most promising processes to combustion sources in the United States is addressed from technical, economic, energy, and environmental standpoints. This effort also includes assessment of the technology for potential regulatory actions.

Assessment of Technology in Japan

Due to stringent emission standards, Japanese technology for control of NO_x and simultaneous control of NO_x and SO_x by flue gas treatment techniques is more advanced than any other country's. EPA has sponsored the publication of periodic reports and papers to facilitate the transfer of information from Japan to the United States. These documents have been mainly prepared by Jumpei Ando of Chuo University, Tokyo, Japan (References 1,2,3). An overview of current Japanese technology, both dry and wet processes for NO_x and NO_x/SO_x control, follows.

Dry NO_x Processes (Reference 3)--

Numerous dry process types are being developed. However, selective catalytic reduction (SCR) processes are the only ones that have achieved notable success in treating combustion flue gas for removal of NO_x and have progressed to the point of being commercially applied. SCR processes are based on the preference of the reaction of ammonia (NH_3) with NO_x rather than other flue gas constituents. Since oxygen (O_2) enhances the reduction, the reactions can best be expressed as:

$$4NH_3 + 4NO + O_2 \xrightarrow{\text{catalyst}} 4N_2 + 6H_2O \qquad (1)$$

$$4NH_3 + 2NO_2 + O_2 \xrightarrow{\text{catalyst}} 3N_2 + 6H_2O \qquad (2)$$

Reaction 1 predominates since approximately 95% of the NO_x in combustion flue gas is in the form of nitrogen oxide (NO). Therefore, a stoichiometric amount of ammonia can be used to reduce NO_x under ideal conditions to harmless molecular nitrogen (N_2) and water vapor (H_2O). An NH_3:NO mole ratio of about 1:1 has typically reduced NO_x emissions by 90% with a leak ammonia rate of less than 20 ppm.

The SCR processes are relatively simple, requiring only a reactor, a catalyst, and an ammonia storage and injection system. Some increase in boiler fan capacity, or possibly an additional fan, may be necessary to account for the increase in pressure drop which may be in the range of 500-700 Pa.

The optimum temperature for the reaction is about 1000°C. However, the catalyst effectively reduces the reaction temperature to the 300-450°C range. To obtain flue gas temperatures in this range and to avoid the requirement for large amounts of reheat, the reactor is usually located between the boiler economizer and the air preheater. Depending on system design, the reactor may be located either before or after the particulate control device.

Many different types of catalyst compositions and configurations have been developed. Initially, catalysts were developed for flue gases without particulate and SO_x concentrations such as from natural gas firing. For these applications, a catalyst of platinum (Pt) on an alumina (Al_2O_3) support material was used. Alumina was poisoned by SO_x, particularly SO_3, in the flue gas. Titanium dioxide (TiO_2) was found to be resistant to SO_x poisoning and to be an acceptable catalyst carrier for applications with SO_x in the flue gas such as from oil or coal firing. The catalyst metals also tend to react with SO_x, especially SO_3. Vanadium compounds were found to be resistant to attack from SO_3 and promote the reduction of NO_x with ammonia. Therefore, many SO_x resistant catalysts are based on TiO_2 and V_2O_5. Other active metals are also used including C, Co, Cr, Cu, Fe, Mn, Mo, Ni, W, their oxides, sulfates, or combinations thereof. However, the exact compositions and constituents of most catalysts are proprietary.

Reactor configurations also vary with the application, primarily to accommodate the different particulate concentrations. For natural gas firing, a fixed, packed bed employing a granular or pellet type catalyst can be used. However, particulates in the gas stream will plug a fixed, packed bed.

For applications with moderate particulate concentrations, a moving bed arrangement can be employed and still utilize the granular or a ring shaped catalyst. (The catalyst is charged from the top of the reactor and moves down intermittently or continuously while the flue gas passes through the catalyst layer in a cross flow direction. The catalyst is discharged from the bottom of the reactor, is screened to remove particulates, and can be regenerated to eliminate any contaminants before being returned to the reactor.) Moving bed reactors can treat gases containing less than about 200 mg/Nm^3 of particulates and are applicable to oil firing. They are also applicable to coal firing if an adequate amount of particulates is removed from the flue gas upstream of the NO_x reactor. In most cases, this would require application of a hot-side electrostatic precipitator (ESP) which is usually more expensive than the more commonly used cold-side ESP.

Parallel flow reactors and catalysts were developed to tolerate relatively high particulate concentrations, such as from coal firing. (Parallel flow indicates that the direction of flue gas is parallel, rather than perpendicular, to the catalyst surface.) Parallel flow designs utilize various catalyst configurations including tubular, metallic and ceramic honeycombs or plates, and parallel passage reactors. The selection of the catalyst and reactor configuration will probably depend on site specific considerations since there are advantages and disadvantages associated with each design.

Even though much progress has been made in catalysts and reactor design, some problems still remain. The catalysts may not be resistant to all contaminants in flue gas. In addition, fine particulates, smaller than about 1 micron, may blind the catalyst surface. Catalyst life needs to be extended from the current guarantees of 1 to 2 years for applications with SO_x and particulates in the gas stream.

One of the major concerns with SCR processes is the formation of solid ammonium sulfate [$(NH_4)_2SO_4$] and liquid ammonium bisulfate (NH_4HSO_4). The problem occurs if SO_3, NH_3, and H_2O are present in sufficient quantities, and the flue gas cools to the formation temperature of $(NH_4)_2SO_4$ and NH_4HSO_4. For example, NH_4HSO_4 will form at 210°C if the flue gas contains 10 ppm of NH_3 and 10 ppm of SO_3. The formation conditions are difficult to avoid since one expects some leak ammonia from a SCR system and some SO_3 from combustion of sulfur containing fuels. In addition, some catalysts tend to promote the oxidation of SO_2 to SO_3; however, this conversion is usually less than 5% of the SO_2 in the flue gas stream.

The biggest problem seems to be deposition of $(NH_4)_2SO_4$ and NH_4HSO_4 on the air preheater. These compounds are highly corrosive and interfere with heat transfer. The problem appears to be most severe with high sulfur oil firing. With low sulfur oils, the SO_3 concentration is too low to cause problems. Early tests with coal indicate that the $(NH_4)_2SO_4$ and NH_4HSO_4 may deposit on the fly ash or be removed from the heat exchanger surface by the erosive action of the fly ash. However, more operating experience on coal-fired sources is needed to quantify the extent of the problem.

Numerous countermeasures have been proposed to minimize the $(NH_4)_2SO_4$ and NH_4HSO_4 problem. The most desirable techniques are to avoid formation. This can be accomplished by reducing the SO_3 and NH_3 in the reactor effluent or increasing the exhaust temperature of the flue gas. Soot blowing and water washing techniques are useful in removing the deposits after formation. Heat exchanger modifications, which increase the effectiveness of the removal techniques or minimize the likelihood of deposit, are also being considered as well as use of corrosion resistant heat exchanger surfaces.

There are numerous developers of SCR processes and numerous pilot, prototype, and commercial scale applications. Table I lists 13 process developers and 62 applications over 10,000 Nm^3/hr (normal cubic meters per hour) along with information on the type of source, fuel, plant size, type of reactor, and start-up date.

The cost of SCR systems varies with process developer and application. However, the Japan Environment Agency has investigated the costs of a SCR application to a new oil-fired, 300 MW installation in Japan. To remove 80% of the NO_x, the capital investment was estimated to be about $15.5/kW and the annualized cost, about 1.6 mills/kWh.

EPA is sponsoring a pilot scale evaluation of SCR technology which will be discussed later in the paper.

Wet NO_x Processes (Reference 3)--

The wet NO_x processes developed to date cannot compete economically with dry SCR processes for removal of NO_x from combustion flue gas. This is primarily due to the complexity, limited applicability, and water pollution problems associated with the wet NO_x processes.

Dry Simultaneous NO_x/SO_x Processes (Reference 3)--

Although there are several dry simultaneous NO_x/SO_x removal systems, the only commercially demonstrated system is the Shell Flue Gas Treating system. This process was originally designed for SO_2 control but was also found to be adaptable for NO_x control.

The process uses copper oxide supported on stabilized alumina placed in two or more parallel passage reactors. The reactions can be expressed as follows:

$$CuO + 1/2\ O_2 + SO_2 \longrightarrow CuSO_4 \tag{3}$$

$$4NO + 4NH_3 + O_2 \xrightarrow{CuSO_4} 4N_2 + 6H_2O \tag{4}$$

$$CuSO_4 + 2H_2 \longrightarrow Cu + SO_2 + 2H_2O \tag{5}$$

$$Cu + 1/2\ O_2 \longrightarrow CuO \tag{6}$$

Flue gas is introduced at 400°C into one of the reactors where the SO_x reacts with copper oxide to form copper sulfate. The copper sulfate and, to a lesser extent, the copper oxide act as catalysts in the reduction of NO_x with ammonia. When the reactor is saturated with copper sulfate, flue gas is switched to a fresh reactor for acceptance of the flue gas, and the spent reactor is regenerated. In the regeneration cycle, hydrogen is used to reduce the copper sulfate to copper, yielding a SO_2 stream of sufficient concentration for conversion to sulfur or sulfuric acid. The copper in the reactor is oxidized, preparing the reactor for acceptance of the flue gas again. Between acceptance and regeneration, steam is injected into the reactor to purge the remaining flue gas or hydrogen to eliminate any possibility of combustion. The process can also be operated in the NO_x-only mode by eliminating the regeneration cycle, or in the SO_x-only mode by eliminating the ammonia injection.

The process has been installed at the Showa Yokkaichi Sekiyu plant in Yokkaichi by Japan Shell Technology, Ltd. on a heavy-oil-fired boiler treating 120,000 Nm^3/hr of flue gas. In this installation, the process removes 90% of the SO_2 and 40% of the NO_x to meet local regulations. The unit has demonstrated 90% SO_2 removal and 70% NO_x removal.

UOP Process Division is the licensor of the process in the United States. Hence, the process will be referred to as the UOP-Shell process in this paper. EPA is sponsoring a pilot scale evaluation of the UOP-Shell process which will be discussed later.

Wet Simultaneous NO_x/SO_x Processes (Reference 3)--

Although the wet NO_x removal processes cannot compete economically with dry NO_x processes, wet simultaneous NO_x/SO_x processes may be competitive with the sequential installation of NO_x control by SCR followed by SO_2 control by flue gas desulfurization (FGD).

The first wet simultaneous NO_x/SO_x systems, called oxidation/absorption/reduction processes, evolved from FGD systems. Since the NO in flue gas is fairly insoluble in aqueous solutions, a gas-phase oxidant is injected before the scrubber to convert NO to the more soluble nitrogen dioxide (NO_2). The absorbent varies with the type of FGD system being modified. The absorbed SO_2 forms a sulfite ion which reduces a portion of the absorbed NO_x to molecular nitrogen. The remaining NO_x are removed from the waste water as nitrate salts. The remaining sulfite ions are oxidized into sulfate by air and removed as gypsum.

The oxidation/absorption/reduction processes have the potential to remove 90% of both SO_x and NO_x from combustion flue gas. However, there are several drawbacks remaining to be overcome before the processes can be widely applied. The process chemistry is complex, and the use of a gas-phase oxidant, such as ozone (O_3) or chlorine dioxide (ClO_2), is expensive. Chlorine dioxide, although cheaper than ozone, adds to the waste water problems created by the nitrate salts.

Absorption/reduction processes were seemingly developed to avoid the use of a gas-phase oxidant. A chelating compound, which has an affinity for the relatively insoluble NO, is added to the scrubbing solution. Ferrous-EDTA (ethylene-diamine tetraacetic acid) has typically been used as the chelating compound. The NO is absorbed into a complex with the ferrous ion and the SO_2 is absorbed as the sulfite ion. The NO complex is reduced to molecular nitrogen by reaction with the sulfite ion. A series of regeneration steps recovers the ferrous chelating compound and oxidizes the sulfite ion into sulfate which is removed as gypsum.

The absorption/reduction processes also have the potential to remove 90% of both the NO_x and SO_x in combustion flue gas. Although the processes seem to have advantages over the oxidation/absorption/reduction processes, there are obstacles to be overcome before the processes can be widely applied. Even with the addition of the chelating compounds, a large absorber is required to absorb the NO. The sum of replacement, recovery, and regeneration costs of the chelating compounds, although potentially less than using the gas-phase oxidants, are still significant. The process chemistry is complex and is sensitive to the flue gas composition of SO_2, NO_x, and oxygen. The molar ratio of SO_2 to NO_x must remain above approximately 2.5 and the oxygen concentration must remain low.

Table II lists the process developers evaluating wet simultaneous NO_x/SO_x technology in Japan. Oxidation/absorption/reduction processes are being investigated by six process developers at nine different sites. For absorption/reduction processes, there are four pilot or bench scale plants currently being operated by four different process developers.

As shown in Table III, based on information from the Japan Environment Agency, it was estimated that a FGD system would have an investment cost of about $77.8/kW with an annualized cost of 6.7 mills/kWh. As stated previously, the cost of a SCR system is \$15.5/kW and 1.6 mills/kWh. However, the cost of a sequential system employing SCR + FGD would be about \$102.8/kW and 8.3 mills/kWh. The total cost increased slightly over the sum of individual SCR and FGD systems to allow for removal of NH_3 from the FGD scrubbing liquor.

The cost of simultaneous NO_x/SO_x, both wet and dry, was estimated to be slightly higher or about \$111.1/kW and 9.4 mills/kWh; however, these cost estimates were more uncertain than the FGD and SCR costs. Costs for all systems were estimated to be about 20% higher for coal-fired sources.

Assessments of Technology for U.S. Application

The Tennessee Valley Authority (TVA), through an interagency agreement with EPA, is developing comparative economics of NO_x and NO_x/SO_x flue gas treatment processes for application in the U.S. This multi-phase study is over 50% complete. Phase I, a technical assessment, was an evaluation and summary of the technical feasibility of all candidate NO_x control processes being offered in the U.S. and Japan. Phase II, a preliminary economic assessment, concentrated on the processes recommended in Phase I for further study. Phase III, a definitive economic assessment, will develop detailed engineering evaluations and cost estimates for the most promising NO_x control cases identified in Phase II. In addition, the impact of application of SCR processes on ammonia availability and cost was evaluated. Phases I and II of the study were cofunded by the Electric Power Research Institute and EPA.

Phase I -- Technical Assessment of NO_x and NO_x/SO_x Processes (Reference 4)--

In Phase I, 42 processes for NO_x and simultaneous NO_x/SO_x control were described. The discussion on each process included the process description, status of development, reported economics, utility and raw material requirements, technical and environmental considerations, and advantages and disadvantages.

In addition, a comparison was made of the dry NO_x and wet simultaneous NO_x/SO_x systems. It was found that, although there are many different types of dry and wet processes, in most cases the dry processes have advantages over the wet processes:

- Low projected capital investment and annual revenue requirements.
- Simple process with few equipment requirements.
- High NO_x removal efficiency (>90%).
- Extensive tests in large units.
- No waste stream generation.

However, the dry systems also have disadvantages:

- Sensitive to inlet particulate levels.
- Require ammonia.
- Possible emission of ammonia and ammonium sulfates and bisulfates.
- Relatively high reaction temperatures (350-400°C).

The wet NO_x/SO_x removal processes have certain general advantages and disadvantages, compared with the dry NO_x systems. The major advantages include:

- Potential economic advantage of simultaneous NO_x/SO_x removal.
- Relatively insensitive to flue gas particulates.
- High SO_2 removal (>95%).

On the other hand, major disadvantages of the wet systems include:

- Expensive processes due to process complexity and insolubility of NO_x in aqueous solutions.
- Formation of nitrates (NO_3^-) and other potential water pollutants.
- Extensive equipment requirements.
- Formation of low-demand byproducts.
- Flue gas reheat required.
- Only moderate NO_x removal.
- Limited application of some processes due to requirement for high SO_x:NO_x ratios.

In addition to being a state-of-the-art review of all NO_x processes undergoing development, one of the main purposes of the study was to identify processes for further evaluation in Phase II of the study. Three criteria were used to screen the processes: technical considerations, developmental status, and representative samples of available technologies. Based on these criteria, the nine processes in Table IV were selected for further study.

Phase II -- Preliminary Economic Estimates (Reference 5)--

The primary purpose of Phase II of the study was to compare the process economics of the different types of NO_x and NO_x/SO_x control techniques on a consistent basis. Preliminary economics, including total capital investment and average annual revenue requirements, were determined. Rigorous comparisons were not made although various conclusions can be drawn from the analysis.

The processes listed in Table IV were evaluated except for the wet NO_x-only process; development of that process was terminated by the developer. However, there appears to be little, if any, future for application of wet NO_x-only processes to combustion sources. The JGC Paranox process, a dry SCR process (NO_x only) employing a parallel passage reactor, was substituted.

Process descriptions, detailed flowsheets, material balances, and a current status of development summary were prepared for each process based on data supplied by the process vendors. Equipment descriptions and costs were prepared from the available data for each process.

Although the study is not complete, preliminary estimates are indicated in Table V. (It must be emphasized that these numbers are subject to change when the study is completed.) However, it is apparent from these estimates that the IHI process, an ozone based system, is not economically attractive. (This finding is consistent with an earlier EPA study (Reference 6) that determined that ozone systems were too expensive for coal-fired applications.) The Moretana Calcium process, a chlorine dioxide based system, and the Asahi process, an EDTA based system, also appear economically unattractive when compared to the least expensive SCR + FGD system, especially based on annual revenue requirements.

Given the uncertainties of the estimates, the comparison of the UOP-Shell dry NO_x/SO_x process and the SCR + FGD system is inconclusive. In addition, it is not apparent which SCR system, moving bed or parallel flow, represents the optimum NO_x-only configuration. The cost estimates for SCR processes include the cost of particulate control by an ESP. The ESP is roughly 40% of the capital cost, which places NO_x control alone at approximately $36/kW.

The study also evaluated energy consumption of the processes, and estimates are given in Table VI. The SCR systems are projected to require less than 0.3% of the boiler capacity. The UOP-Shell, dry NO_x/SO_x process requires the least energy of any NO_x and SO_x system due to reclamation of heat from the byproduct streams. The combination of SCR and FGD is next; the wet NO_x/SO_x systems require significantly higher quantities of energy.

The economic sensitivity of the SCR systems to the cost of ammonia has been the subject of some concern. It was found that the annual ammonia cost was below 12% of the average annual revenue requirements for the dry systems. Therefore, the average annual revenue requirement may be expected to increase about 10% if the ammonia cost is doubled.

Phase III -- Definitive Economic Estimates--

In Phase III of the study, to begin immediately following completion of Phase II, a definitive-level design and economic evaluation of the leading NO_x control techniques will be performed. The study will encompass both flue gas treatment and combustion modification techniques, which will be analyzed individually as well as in combination. This will enable a comparison of 90% NO_x control by flue gas treatment alone and combustion modification followed by flue gas treatment. In addition, dry simultaneous NO_x/SO_x systems will be evaluated against the optimum highly efficient NO_x control system used in conjunction with a conventional FGD unit.

In the course of the study, the bases for conceptual designs will be identified, a definitive engineering package will be prepared, and capital investment and revenue requirements will be estimated. The final report on Phase III is scheduled to be available in early 1980.

Impact of Ammonia Utilization (Reference 7)--

A major concern of the widespread utilization of ammonia-based NO_x control systems has been the impact on the domestic ammonia market. It has been speculated that severe disruptions in the availability and price of ammonia would occur if SCR systems are employed; this could also impact on the availability and cost of ammonia-based fertilizers. In addition, the impact on natural gas, the primary feedstock for ammonia production, was unclear. A study of the situation was undertaken by TVA to address these concerns in parallel with the three-phase technical and economic evaluation discussed above.

The annual NH_3 requirements for a 500 MW coal- and oil-fired boiler were calculated for application of a 90% NO_x removal system based on SCR technology. At an assumed NH_3:NO_x mole ratio of 1.05:1, the NH_3 consumption rates were 5.7 Gg/yr (6300 tons/yr) and 1.6 Gg/yr (1800 tons/yr) for the coal- and oil-fired units, respectively.

From these calculations it is apparent that even a large coal-fired power plant could not justify a captive NH_3 plant since the minimum plant capacity for economic production of NH_3 is about 300 Gg/yr (330,000 tons/yr). Therefore, NH_3 would be purchased from an off-site NH_3 plant and stored in tanks at the power plant.

The projected U.S. electrical generating capacity was estimated for the period from 1975 to 2000. Assuming application of a SCR system removing 90% of the NO_x to all new large industrial and utility boilers ($\geq$260 GJ/hr or 250 x 10^6 Btu/hr) beginning in 1985, the NH_3 demand for NO_x control was determined. The ammonia supply to meet both the conventional NH_3 demand and annual growth of this demand for NO_x control was projected using an assumed annual growth rate for ammonia production of 3.0%. It was found that the NH_3 demand for NO_x control ranged from 0.6% of the total NH_3 supply in 1985 to 20-25% in the year 2000.

Thus, although requiring substantial amounts of NH_3 in the future, the need for NH_3 for NO_x control apparently would not have an abrupt adverse impact on the availability and price of NH_3. Under the assumptions of the study, the primary impact on the domestic NH_3 market would be to cause the U.S. NH_3 demand to increase at 4.5%/yr during the period 1985-2000 rather than the assumed 3.0%. This increase could be met with the addition of one ammonia plant per year. In addition, although use of natural gas is counter to the National Energy Plan, utilization of NH_3 for NO_x control should not adversely affect the price and availability of natural gas.

Assessment of Technology for an Industrial Boiler NSPS

IERL-RTP is sponsoring a series of studies to determine the applicability of various emission control technologies to industrial boilers. The primary purpose of these studies is to support the development of a new source performance standard (NSPS) for industrial boilers. The following technologies are being considered:

- Oil Cleaning and Existing Clean Oil
- Coal Cleaning and Existing Clean Coal
- Synthetic Fuels
- Fluidized Bed Combustion
- NO_x Combustion Modification
- NO_x and NO_x/SO_x Flue Gas Treatment
- Flue Gas Desulfurization
- Particulate Control

Following completion of reports on the individual technologies, a comprehensive assessment report will be prepared which discusses how the technologies should be integrated for optimum multi-pollutant control. Subsequently, EPA's Office of Air Quality Planning and Standards (OAQPS) will study the impact of various control options. These studies will ultimately lead to the establishment of a NSPS for industrial boilers. Acurex Corporation is the contractor assisting OAQPS and IERL-RTP in this overall effort.

As shown above, NO_x and NO_x/SO_x flue gas treatment processes are among the technologies being considered. Radian Corporation is preparing the technology assessment report on these processes. The report will contain the following sections:

- Emission Control Techniques
- Candidates for Best System of Emission Reduction
- Control System Costs

- Energy Considerations
- Environmental Considerations
- Emission Source Test Data

The cost, energy, and environmental considerations will be based on standard boilers listed in Table VII. The coal-fired boilers will be analyzed for high and low sulfur Eastern coal and low sulfur Western coal cases.

The final report on the assessment of NO_x and NO_x/SO_x technologies should be available in the spring of 1979. The comprehensive assessment report on optimum multi-pollutant control systems should be available in the Fall of 1979. (Note that consideration of a technology for a standard does not imply that the ultimate standard will be based on that technology.)

CONTROL STRATEGY ASSESSMENT STUDIES

While the primary purpose of the technology assessment studies is to determine the performance of the technology, the primary objective of the control strategy assessment studies is to determine if and when the technology will be needed in the U.S. Recent studies in this area have utilized computer modeling techniques to evaluate alternative control strategies and investigated the issues (such as prevention of significant deterioration) which could eventually require increased NO_x control.

Assessment of Point Source Impact on Ambient NO_2 Levels (Reference 8)

A study was undertaken for EPA by Radian Corporation to determine the impact of various stationary source NO_x control strategies on attaining and maintaining the National Ambient Air Quality Standard (NAAQS) for NO_2. The Chicago Air Quality Control Region (AQCR) was selected for use in this study since it has historically encountered ambient NO_x problems.

Annual Impact--

The original purpose of the study was to determine the effect on annual average ambient NO_2 levels of applying NO_x control technology to large point sources ($\geq$ 105 GJ/hr or 100 X 10^6 Btu/hr) in the AQCR. A dispersion model was used to relate NO_x emissions to ambient NO_2 concentrations in Chicago.

It was found that, although the major point sources account for nearly 40% of the total NO_x emissions in Chicago, they account for less than 10% of the ambient NO_2 levels, on the average. Considering major point source "hotspots" (i.e., localized areas of the city where major point source impact is the greatest), modeling results indicate that these sources account for 12% of a predicted NO_2 level of about 60 $\mu g/m^3$. Taking a worst-case approach and assuming that all NO_x emissions from major point sources are converted to NO_2, it was found that the predicted cumulative impact of all major point sources at locations of maximum annual impact is still only 15% of the standard.

Therefore, it was concluded that total removal of large point source NO_x emissions would result in only a small improvement in annual average NO_2 air quality in Chicago, and control of large point sources alone would not be adequate to achieve and maintain the annual average NAAQS.

Short-term Impact--

Based on the Clean Air Act Amendments of 1977 and the possible establishment of a short-term NAAQS, this Radian study was expanded to investigate the effect of NO_x control techniques on short-term ambient concentrations in the AQCR for present and future years. Standards were assumed of 250, 500, 750, and 1000 $\mu g/m^3$ of NO_2 based on a 1 hour average.

The short-term impact assessment was made using Gaussian-type dispersion models. A significant part of the effort of this study was directed toward defining the short-term NO_x emission rates that should be used in the model. This was done primarily by adjusting the annual average emission rates. Adjustments were made for season of the year, day of the week, and time of day. The entire emissions inventory for the Chicago AQCR, including vehicular and other area sources, was modeled using this approach.

The computer-predicted ambient NO_x concentrations were converted to ambient NO_2 concentrations by applying a ratio of NO_2 to NO_x determined from measured air quality data in Chicago. This ratio is a function of season of the year and time of day; ratios used in the study varied from 0.25 to 0.5. The accuracy of this approach is not known since several photochemical reactions are involved in the conversion of NO_x to NO_2 and other species. For assessment of future year impacts, the growth in NO_x emissions was estimated.

The study found that individual large point sources may account for 60% of a predicted 1 hour NO_2 concentration of 1100 $\mu g/m^3$ in industrial areas and 90% of a level of 800 $\mu g/m^3$ in non-industrial areas. This indicates that controlling large point sources may provide significant improvements in short-term NO_2 air quality. However, the degree of control required is highly dependent on any short-term NO_2 NAAQS adopted by EPA. The results summarized in Table VIII show the percentage of the 14 largest existing point sources which would require controls for various standard levels if those standards were currently in effect. It was assumed that the more cost effective combustion modification techniques would be employed first, and that the flue gas treatment techniques would only be applied if necessary to maintain the established ambient level.

The percentages of Table VIII are based on individual large point source impacts added to the impacts of other point sources, vehicular sources, and non-vehicular area sources. When large point sources are located near each other so that their impacts interact, the degree of control required increases significantly and more flue gas treatment is required.

Projections for NO_x emissions to 1985 indicate that the same level of control as shown in Table VIII would be required. There are two reasons for this unexpected result. First, the highest predicted short-term concentrations are dominated by large point sources to the extent that changes in the impacts from other sources do not make a large difference. Second, the change in impact of other sources by 1985 is small because increases in non-vehicular emissions are counterbalanced by the decrease in projected vehicular emissions.

It is concluded that control of large point source NO_x emissions would result in a significant improvement in short-term NO_2 air quality and may be necessary to attain and maintain compliance with a short-term NAAQS.

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concerning both future NO_x emission reduction requirements and the ultimate effectiveness of alternative NO_x control methods such as combustion modification.

EXPERIMENTAL PROJECTS

The technology assessment and control strategy studies and financial constraints aid in determining the number and scale of experimental projects. These studies, as well as previous experimental projects, supported a jump to pilot scale evaluations of NO_x and NO_x/SO_x processes on a coal-fired application. Previous experimental projects included laboratory projects on development of catalysts for NO_x reduction with ammonia (References 10, 11), a pilot-scale project evaluating a selective catalytic reduction process on a gas-fired application (Reference 12), and a laboratory evaluation of NO_x reduction with metal sulfides (Reference 13).

After solicitation and evaluation of proposals from interested parties, EPA awarded two contracts in May 1978 for the pilot-scale evaluation of flue gas treatment technology on a coal-fired source. One contract went to Hitachi Zosen for demonstration of NO_x removal and the other went to UOP Process Division for demonstration of simultaneous NO_x/SO_x removal.

Both pilot plant projects have similar objectives and scope. The basic objective is to demonstrate the feasibility of the processes for highly efficient control of NO_x or NO_x/SO_x on a coal-fired source. Pollutant removal efficiencies of 90% are expected.

The scope of the projects is divided into four phases:

I - Design
II - Procurement and erection
III - Startup, debugging, and optimization
IV - Long term operation and assessment.

The design phases were completed within approximately 3 months of contract award on both projects. Procurement and erection, Phase II, is expected to require about 9 months to complete. Phase III, which will require 4-8 months to complete with the majority of time spent on optimization testing, will contain a parametric study of process variables including: flow rate, temperature, NH_3:NO ratio, and NO_x, SO_2, SO_3, and particulate concentrations. Long-term operation and assessment will be conducted during a 90 day continuous run in Phase IV.

Project manuals will be available on both projects in early 1979. The final reports on the results of the projects should be available in mid-1980.

Hitachi Zosen NO_x Pilot Plant (Reference 14)

Hitachi Zosen's NO_x removal process is based on SCR technology. Since these processes were discussed previously in the paper, only key process features will be discussed further.

Hitachi Zosen utilizes a metallic honeycomb catalyst arrangement for applications with high particulate and SO_x concentrations. The reactor is located between the boiler economizer and the air preheater and in front of any particulate control device. The reaction temperature is in the range of 350-420°C. The pressure drop is about 200-500 Pa. For 90% NO_x reduction, a NH_3:NO mole ratio of 1:1 is used.

The process will be evaluated on a pilot plant scale ($\sim$2000 Nm^3/hr) on a coal-fired source. The host site for the pilot plant will be Georgia Power Company's Plant Mitchell near Albany, Georgia. Flue gas will be obtained from Unit 3, a pulverized coal-fired Combustion Engineering boiler with a nameplate rating of 125 MW.

Envirotech/Chemico Air Pollution Control Corporation (CAPCC), Hitachi Zosen's American licensee, will be the major subcontractor on the project. CAPCC will provide detailed engineering, design, procurement, erection, and operation of the pilot plant in cooperation with Hitachi Zosen. Fabrication and procurement will be done within the U.S. as far as possible.

UOP-Shell NO_x/SO_x Pilot Plant (Reference 15)

The UOP-Shell dry NO_x/SO_x removal system is based on the Shell Flue Gas Treating process which has also been discussed previously in the paper. Briefly, the process employs a parallel passage reactor using CuO as the sorbent for SO_2 and $CuSO_4$ as the catalyst for the reduction of NO_x with NH_3. The reactor is located between the boiler economizer and the air preheater and in front of any particulate control device. The process operates at a temperature of 400°C during both acceptance and regeneration cycles. The cycles will be controlled for 90% removal of both NO_x and SO_2. For 90% NO_x reduction, a NH_3:NO mole ratio of 1:1 is used.

The process will be evaluated on a pilot plant scale ($\sim$2000 Nm^3/hr) on a coal-fired source. An existing pilot plant, previously used by UOP to evaluate SO_2 removal, will be modified for simultaneous removal of NO_x and SO_2. The host site for the pilot plant will be Tampa Electric Company's Big Bend Station in North Ruskin, Florida. Flue gas can be obtained from Unit 1 or 2, which are Riley-Stoker pulverized coal-fired boilers with a nameplate rating of 400 MW each.

CONCLUSIONS

This paper has summarized the status of NO_x and NO_x/SO_x flue gas treatment technology and presented the results of recent EPA studies of the technology. The following conclusions can be drawn.

1. Dry NO_x processes, based on selective catalytic reduction (SCR) of NO_x with ammonia, can remove 90% of the NO_x from the flue gas of combustion sources.
2. SCR processes have been extensively demonstrated on commercial-scale gas- and oil-fired sources in Japan.
3. Based on the experience in Japan, SCR processes can be expected to be successfully applied to gas- and oil-fired sources in the U.S.
4. Reactors and catalysts for SCR systems have been developed to tolerate high SO_x and particulate concentrations and are ready for test application on coal-fired sources in the U.S. and Japan.
5. The formation of ammonium sulfate and bisulfate remains a problem for SCR systems, but solutions are being investigated.
6. Wet processes cannot economically compete with SCR processes for control of NO_x.
7. The UOP-Shell process warrants further evaluation as a dry simultaneous NO_x/SO_x control system.
8. Wet simultaneous NO_x/SO_x processes currently appear to be less attractive than the sequential control of NO_x and SO_x by SCR and flue gas desulfurization.
9. The energy consumption of SCR processes is less than 0.3% of station capacity.

10. The widespread application of SCR processes is not expected to have an abrupt adverse impact on the domestic ammonia market.

11. NO_x and NO_x/SO_x flue gas treatment processes warrant consideration as the basis for a New Source Performance Standard for industrial boilers.

12. Large point sources do not have a significant impact on annual average ambient NO_2 levels.

13. Large point sources may have a significant impact on short term ambient NO_2 levels.

14. NO_x flue gas treatment processes may be needed to attain and maintain compliance with EPA ambient standards in certain Air Quality Control Regions.

15. EPA's pilot plant project with Hitachi Zosen will enable evaluation of a SCR process for 90% control of NO_x on a coal-fired source.

16. EPA's pilot plant project with UOP Process Division will enable evaluation of a dry simultaneous NO_x/SO_x process for 90% control of both NO_x and SO_2 on a coal-fired source.

17. EPA experimental projects, in conjunction with technology assessment and control strategy studies, will enable an assessment of the feasibility of NO_x and NO_x/SO_x flue gas treatment processes for application in the U.S.

REFERENCES

1. Ando, Jumpei, Katsuya Nagata, and B. A. Laseke. *NO_x Abatement for Stationary Sources in Japan*. PEDCO Environmental, Inc., EPA-600/7-77-103b (NTIS No. 276-948), September 1977. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

2. Ando, Jumpei. *SO_2 Abatement for Stationary Sources in Japan*. EPA-600/7-78-210, November 1978. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

3. Ando, Jumpe , and Katsyua Nagata. *NO_x Abatement for Stationary Sources in Japan*. (Draft Report; to be published January 1979 by EPA.)

4. Faucett, H. L., J. D. Maxwell, and T. A. Burnett. *Technical Assessment of NO_x Removal Processes*. Tennessee Valley Authority, EPA-600/7-77-127 (NTIS No. 276-637, EPRI No. AF-568, TVA No. Y-120), November 1977. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

5. Burnett, T. A., J. D. Maxwell, and H. L. Faucett. *The Preliminary Economics of Alternative NO_x Flue Gas Treatment Processes*. Tennessee Valley Authority. (12/78 Draft Report; to be published early 1979 by EPA and EPRI.)

6. Harrison, J. W. *Technology and Economics of Flue Gas NO_x Oxidation by Ozone*. Research Triangle Institute, EPA-600/7-76-033 (NTIS 261 917), December 1976. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

7. Burnett, T. A., and H. L. Faucett. *Impact of Ammonia Utilization by NO_x Flue Gas Treatment Processes*. Tennessee Valley Authority, EPA-600/7-79-011, January 1979. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

8. Eppright, B. R., E. P. Hamilton, III, M. A. Haecker, and Carl-Heinz Michelis. *Impact of Point Source Control Strategies on NO_2 Levels*. Radian Corporation, EPA-600/7-78-212, November 1978. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

9. Corbett, W. E., G. D. Jones, W. C. Micheletti, R. M. Wells, and G. E. Wilkins. *Assessment of the Need for NO_x Flue Gas Treatment Technology*. Radian Corporation, EPA-600/7-78-215, November 1978. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

10. Nobe, K., G. L. Bauerle, and S. C. Wu. Parametric Studies of Catalysts for NO_x Control from Stationary Power Plants. University of California, Los Angeles, EPA-600/7-76-026 (NTIS No. PB 261 289), October 1976. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

11. Koutsoukos, E. P., J. L. Blumenthal, M. Ghassemi, and G. L. Bauerle. Assessment of Catalysts for Control of NO_x from Stationary Power Plants. TRW, Inc., EPA-650/2-75-001a (NTIS No. PB 239 745), January 1975, U.S. Environmental Protection Agency, Research Triangle Park, N.C.

12. Kline, J. M., P. H. Owen, and Y. C. Lee. Catalytic Reduction of Nitrogen Oxides with Ammonia: Utility Pilot Plant Operation. Environics, Inc., EPA-600/7-76-031 (NTIS No. PB 261 265), October 1976. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

13. McCandless, F. P., and Kent Hodgson. Reduction of Nitric Oxide with Metal Sulfides. Montana State University, EPA-600/7-78-213, November 1978. U.S. Environmental Protection Agency, Research Triangle Park, N.C.

14. Wiener, R. S., and Rafat R. Morcos, Project Manual: Evaluation of Hitachi Zosen NO_x Flue-Gas Treatment Process. Chemico Air Pollution Control Company. (Draft Report; to be published January 1979 by EPA.)

15. Pohlenz, J. B., and Nooy, F. M. Project Manual: Evaluation of UOP-Shell NO_x/SO_x Flue Gas Treatment Process. UOP Process Division. (Draft Report; to be published in January 1979 by EPA.)

TABLE I. SELECTIVE CATALYTIC REDUCTION PLANTS IN JAPAN

Process Developer	Gas Source	Fuel[a]	Capacity (Nm^3/hr)	Type of Reactor[b]	Start-up
Asahi Glass	Furnace	--	70,000	IMB	--
Hitachi, Ltd.	Coke Oven	COG	500,000	IMB	Nov. 1976
Hitachi, Ltd.	Boiler	HO(HS)	15,000	IMB	Oct. 1977
Hitachi, Ltd.	Boiler	Kerosene	16,000	FB	Oct. 1977
Hitachi, Ltd.	Boiler	HO(LS)	20,000	FB	Aug. 1977
Hitachi, Ltd.	Boiler	HO(LS)	19,000	FB	July 1977
Hitachi, Ltd.	Boiler	Crude Oil	300,000	FB	July 1977
Hitachi, Ltd.	Boiler	LNG	2,000,000x2	FB	Apr. 1978
Hitachi, Ltd.	Boiler	HO	20,000	IMB	Apr. 1978
Hitachi, Ltd.	Boiler	Kerosene	30,000	FB	Dec. 1978
Hitachi, Ltd.	Boiler	HO(LS)	490,000	PPC	June 1978
Hitachi, Ltd.	Boiler	HO(LS)	550,000	PPC	June 1978
Hitachi Zosen	Boiler	CO	350,000	FB	Oct. 1975
Hitachi Zosen	Boiler	HO(HS)	440,000	FB	Nov. 1975
Hitachi Zosen	Furnace	Kerosene	71,000	FB	May 1976
Hitachi Zosen	Furnace	Coke, Oil	762,000	FB	Nov. 1976
Hitachi Zosen	Furnace	HO	10,000	FB	Dec. 1976
Ishikawajima H.I.	Boiler	Crude Oil	20,000	HC	Apr. 1977
Ishikawajima H.I.	Boiler	HO(LS)	180,000	HC	Jan. 1978
Ishikawajima H.I.	Boiler	HO(LS)	960,000	HC	Apr. 1978
Ishikawajima H.I.	Boiler	HO(LS)	480,000	HC	June 1978
Ishikawajima H.I.	Boiler	Crude Oil	1,000,000	HC	Apr. 1979
Ishikawajima H.I.	Boiler	HO(LS)	1,900,000	HC	July 1979
Ishikawajima H.I.	Boiler	HO(LS)	1,660,000	HC	Aug. 1981
JGC	Furnace	HO(MS)	50,000	PPR	Nov. 1975
JGC	Boiler	CO	70,000	PPR	July 1976
JGC	Coke Oven	COG	150.000	PPR	Mar. 1977
Kobe Steel	Coke Oven	COG	104,000	IMB	Aug. 1977
Kurabo	Boiler	HO(HS)	30,000	CMB	Aug. 1975
Mitsubishi H.I.	Boiler	HO(LS)	300,000	IMB	Sept.1976
Mitsubishi H.I.	Boiler	LNG	15,000x2	FB	Dec. 1976

(Continued)

TABLE I (Continued). SELECTIVE CATALYTIC REDUCTION PLANTS IN JAPAN

Process Developer	Gas Source	Fuel[a]	Capacity (Nm^3/hr)	Type of Reactor[b]	Start-up
Mitsubishi H.I.	Boiler	HO(LS)	40,000	PPC	Mar. 1977
Mitsubishi H.I.	Boiler	HO(LS)	200,000	HC	Jan. 1978
Mitsubishi H.I.	Boiler	LNG	1,690,000x2	FB	Oct. 1978
Mitsubishi H.I.	Boiler	HO(LS)	1,010,000	PPC	Feb. 1978
Mitsubishi H.I.	Boiler	HO(LS)	490,000	PPC	July 1978
Mitsubishi H.I.	Boiler	HO(LS)	1,920,000	HC	Feb. 1980
Mitsubishi Kakoki	Boiler	HO(HS)	14,000	FB	July 1978
Mitsubishi Kakoki	Furnace	Naphtha	19,000	FB	Oct. 1978
Mitsubishi Kakoki	Boiler	Kerosene	10,000	FB	Nov. 1978
Mitsubishi Kakoki	Boiler	Kerosene	30,000	FB	Oct. 1977
Mitsubishi Kakoki	Boiler	Kerosene	43,000	FB	Oct. 1978
Mitsui Engineering	Boiler	CO	200,000	FB	Oct. 1975
Mitsui Engineering	Boiler	HO(LS)	220,000	TC	Apr. 1978
Mitsui Toatsu	Furnace	Off Gas	87,000	FB	Feb. 1976
Mitsui Toatsu	Furnace	Off Gas	91,000	FB	Sept. 1976
Mitsui Toatsu	Furnace	Off Gas	170,000	FB	Jan. 1977
Mitsui Toatsu	Furnace	Off Gas	363,000	FB	June 1977
Mitsui Toatsu	Boiler	Off Gas	300,000	FB	Oct. 1977
Sumitomo Chemical Co.	Boiler	HO(HS)	30,000	FB	July 1973
Sumitomo Chemical Co.	Furnace	LPG	200,000	FB	May 1974
Sumitomo Chemical Co.	Furnace	LPG	250,000	FB	Jan. 1975
Sumitomo Chemical Co.	Furnace	LPG	200,000	FB	Apr. 1975
Sumitomo Chemical Co.	Furnace	LPG	200,000	FB	Apr. 1975
Sumitomo Chemical Co.	Furnace	LPG	100,000	FB	--
Sumitomo Chemical Co.	Furnace	LPG	10,000	FB	--
Sumitomo Chemical Co.	Boiler	HO(MS)	240,000	FB	Mar. 1976
Sumitomo Chemical Co.	Boiler	HO(MS)	300,000	IMB	Oct. 1976
Sumitomo Chemical Eng.	Boiler	Naphtha	31,000x2	FB	Oct. 1977
Sumitomo Chemical Eng.	Boiler	Naphtha	23,000	FB	Dec. 1977
Sumitomo Chemical Eng.	Boiler	Naphtha	23,000	FB	June 1978
Sumitomo Chemical Eng.	Boiler	Naphtha	19,000	FB	July 1978

(Continued)

TABLE I (Continued). SELECTIVE CATALYTIC REDUCTION PLANTS IN JAPAN

Source: Reference 3

a. Fuel Codes

CO	Carbon Monoxide
COG	Coke Oven Gas
HO	Heavy Oil
HO(HS)	High Sulfur Heavy Oil
HO(LS)	Low Sulfur Heavy Oil
HO(MS)	Medium Sulfur Heavy Oil
LNG	Liquefied Natural Gas
LPG	Liquefied Propane Gas

b. Reactor Codes

CMB	Continuous Moving Bed
FB	Fixed Bed
HC	Honeycomb Catalyst
IMB	Intermittent Moving Bed
PPC	Parallel Plate Catalyst
PPR	Parallel Passage Reactor
TC	Tubular Catalyst

TABLE II. WET NO_X/SO_X CONTROL PLANTS IN JAPAN

Process Developer	Capacity (Nm^3/hr)	Source of Gas	Start-up
OXIDATION/ABSORPTION/REDUCTION PROCESSES			
Chiyoda	1,000	Oil-fired Boiler	Aug. 1973
Ishikawahima H.I.	5,000	Oil-fired Boiler	Sep. 1975
Mitsubishi H.I.	2,000	Oil-fired Boiler	Dec. 1974
Osaka Soda	60,000	Oil-fired Boiler	Mar. 1976
Shirogane	48,000	Oil-fired Boiler	Aug. 1974
Sumitomo Metal-Fujikasui	62,000	Oil-fired Boiler	Dec. 1973
Sumitomo Metal-Fujikasui	100,000	Heating Furnace	Dec. 1974
Sumitomo Metal-Fujikasui	39,000	Oil-fired Boiler	Dec. 1974
Sumitomo Metal-Fujikasui	25,000	Sintering Machine	-- 1976
ABSORPTION/REDUCTION PROCESSES			
Asahi Chemical	600	Oil-fired Boiler	Apr. 1974
Chisso Corp.	300	Oil-fired Boiler	Apr. 1974
Kureha Chemical	5,000	Oil-fired Boiler	Apr. 1975
Mitsui S.B.	150	Oil-fired Boiler	Apr. 1974

Source: Reference 3

TABLE III. COSTS OF NO_x AND NO_x/SO_x CONTROL SYSTEMS IN JAPAN

Process Type	Pollutant Removed	Capital Cost		Operating Costs	
		¥/kW	$/kW	¥/kWh	mills/kWh
Selective Catalytic Reduction (SCR)	NO_x	2800	15.5	0.3	1.6
Flue Gas Desulfurization (FGD)	SO_2	14000	77.8	1.2	6.7
SCR + FGD	NO_x & SO_2	18500	102.8	1.5	8.3
Simultaneous NO_x/SO_x (Dry and Wet)	NO_x & SO_2	20000	111.1	1.7	9.4

Basis for estimate:

Plant Size	300 MW, new	Maintenance	3% of investment cost
Fuel	oil	Insurance	2% of investment cost
NO_x Concentration	200 ppm	Overhead	5% of investment cost
SO_x Concentration	1500 ppm	Catalyst Life	2 years
Particulate Concentration	200 mg/Nm^3	Annual Operation	8000 hours
Temperature	380°C	Ammonia	¥80/kg
NO_x Removal Efficiency	80%	Power	¥12/kWh
SO_2 Removal Efficiency	90%	Steam	¥2/kg
Depreciation	7 years	Kerosene	¥32/kg
Interest Per Year	10%	Monetary Conversion Rate	¥180/$

Source: Information from hearings of the Japan Environment Agency as reported in Reference 3.

TABLE IV. PROCESSES RECOMMENDED FOR FURTHER STUDY UNDER THE EPA/EPRI/TVA ASSESSMENT PROJECT

Process	Type of Process (classification)
UOP-Shell	Dry Simultaneous SO_2/NO_x (Selective catalytic reduction of NO_x and sorption of SO_2 with CuO)
UOP-Shell	Dry NO_x only (Selective catalytic reduction: parallel passage reactor)
Hitachi Zosen	Dry NO_x only (Selective catalytic reduction: metallic honeycomb reactor)
Kurabo Knorca	Dry NO_x only (Selective catalytic reduction: moving bed reactor)
JGC Paranox[a]	Dry NO_x only (Selective catalytic reduction: parallel passage reactor)
Moretana Calcium	Wet Simultaneous SO_2/NO_x (Oxidation/absorption/reduction: chlorine dioxide as oxidant)
Ishikawajima H.I. (IHI)	Wet Simultaneous SO_2/NO_x (Oxidation/absorption/reduction: ozone as oxidant)
Asahi Chemical	Wet Simultaneous SO_2/NO_x (Absorption/reduction: ferrous-EDTA as chelating compound)
MON Alkali Permanganate[b]	Wet NO_x only

Source: Reference 4

[a] Not initally recommended; added as a substitute for the wet NO_x only process.

[b] Development discontinued by the process developer; hence, the process was subsequently dropped from the recommended list.

TABLE V. COSTS OF NO_x AND NO_x/SO_x SYSTEMS IN THE U.S.

Process Type	Pollutant Removed	Capital Cost ($/kW)	Revenue Requirement (mills/kWh)
Selective Catalytic Reduction (SCR)	NO_x, Part.	>60	>2.2
Flue Gas Desulfurization (FGD)	SO_2	100	4.2
SCR + FGD	NO_x, SO_2, Part.	>160	>6.4
Dry, Simultaneous (UOP-Shell)	NO_x, SO_2, Part.	>155	>5.7
Wet, Simultaneous	NO_x, SO_2, Part.		
Moretana (ClO_2)		>180	>11.0
Asahi (EDTA)		>200	>11.0
IHI (Ozone)		>380	>16.0

Basis for the Estimate:

Particulate Control System	ESP for dry systems; wet scrubber for wet simultaneous systems
FGD System	Limestone
SO_2 Removal Efficiency	90%
NO_x Removal Efficiency	90%
Particulate Removal Efficiency	99.5%
Boiler Size	500 MW, new
Fuel	Coal
Heating value	24.4 MJ/kg (10,500 Btu/lb)
Sulfur content	3.5%
Ash content	16%
Operation	7000 hr/yr
Capital Investment	mid-1979
Annual Revenue Requirement	mid-1980

Source: Preliminary results from Reference 5.

TABLE VI. COMPARISON OF ENERGY REQUIREMENTS FOR VARIOUS NO_x AND NO_x/SO_x PROCESSES

Process Type	Pollutant Removed	% of boiler capacity[a]
Selective Catalytic Reduction (SCR)	NO_x, Part.	~0.3
Flue Gas Desulfurization (FGD)	SO_2	3.4
SCR + FGD	NO_x, SO_2, Part.	~3.7
Dry Simultaneous (UOP-Shell)	NO_x, SO_2, Part.	~0.6[b]
Wet Simultaneous	NO_x, SO_2, Part.	
Moretana (ClO_2)		~8.1
Asahi (EDTA)		~11.3
IHI (Ozone)		~18.6

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[a] Basis for the estimate: See Table V

[b] Includes heat credit for byproduct streams

Source: Reference 5.

TABLE VII. STANDARD BOILERS SELECTED FOR EVALUATION

Boiler Type	Fuel	Thermal Input GJ/hr	Thermal Input (10^6 Btu/hr)
Package, Scotch firetube	Natural gas	15.8	15.0
Package, Scotch firetube	Distillate oil	15.8	15.0
Package, watertube	Residual oil	158.2	150.0
Package, watertube, underfeed	Stoker coal	31.6	30.0
Field-erected, watertube, chain grate	Stoker coal	79.1	75.0
Field-erected, watertube, spreader	Stoker coal	158.2	150.0
Field-erected, watertube	Pulverized coal	210.9	200.0

TABLE VIII. CONTROL REQUIRED OF THE 14 LARGEST POINT SOURCES IN CHICAGO TO COMPLY WITH A SHORT-TERM NAAQS

Short-Term NAAQS ($\mu g/m^3$)	Percentage of Plants Requiring		
	No Control	Moderate Control[a]	High Control[b]
1000	79	21	0
750	36	64	0
500	14	57	29
250	0	7	93

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[a] Combustion modification (~50% NO_x control)

[b] Flue gas treatment or combustion modification plus flue gas treatment (~90% NO_x control)

Source: Reference 8.

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CHEMILUMINESCENT MEASUREMENT OF NITRIC OXIDE IN COMBUSTION PRODUCTS

By:

Blair A. Folsom
Craig W. Courtney
Energy and Environmental Research Corporation
Santa Ana, California 92705

ABSTRACT

The response of commercially-available chemiluminescent NO_x analyzers to simulated combustion products containing NO was investigated. An accurate flow metering system was used to combine O_2, CO_2, CO, N_2, Ar, H_2O, CH_4, and H_2 into simulated combustion products modeling a wide range of fuels and excess air conditions. The simulated combustion products were doped with known amounts of NO and then monitored by two commercial chemiluminescent NO_x analyzers.

The results indicate that chemiluminescent analyzers spanned with NO/N_2 generally indicate less than the actual amount of NO in sampled combustion products. The errors range from one to 20 percent depending upon fuel type, oxidant composition and the sample conditioning system.

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SECTION 1

INTRODUCTION

The measurement of nitric oxide (NO) concentrations in combustion products by chemiluminescence has several advantages over alternative methods(1,2,3) and as a result the chemiluminescent NO analyzer (CLA) has become a standard instrument for most laboratory and field emission tests. The usual procedure for CLA calibration is to set the instrument zero and span with high purity nitrogen (N_2) and a known concentration of NO in N_2 respectively. The instrument is then used to measure NO in combustion products. Ideally the composition of the combustion products, which varies according to fuel type and excess air level, will not affect the measurement of NO. However, several investigators have found that background gas composition can measurably affect the NO concentration indicated by a CLA.(3,4,5) Extrapolating these results to typical combustion product compositions indicates that the common procedure of neglecting background gas composition variations could introduce errors as large as 28% in indicated NO concentrations.(5) The objectives of this study were to:

- Assess the accuracy of commercial CLAs measuring NO in combustion products following the procedures recommended by the instrument manufacturers
- Examine methods of correcting CLA indicated NO concentrations for the effects of background gas composition variations
- Examine methods to improve calibration procedures

Two commercially available CLAs were zeroed and spanned with N_2 and NO in N_2 respectively and then used to measure known concentrations of NO in a variety of background gases simulating combustion products from a wide range of fuel compositions and combustor operating conditions. Binary mixtures were also tested. The NO concentrations indicated by the CLAs were then compared with the actual NO concentrations to determine the effects of background gas composition.

SECTION 2

CHEMILUMINESCENT MEASUREMENT OF NO

The chemiluminescent measurement of NO is based upon the following four reactions:

$$NO + O_3 \longrightarrow NO_2^* + O_2 \qquad (1)$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (2)$$

$$NO_2^* \longrightarrow NO_2 + h\nu \qquad (3)$$

$$NO_2^* + M \longrightarrow NO_2 + M \qquad (4)$$

Nitric oxide and ozone (O_3) react readily to form nitrogen dioxide (NO_2) in either an excited state (NO_2*) or a ground level state (NO_2). The yield of NO_2* is about 10% at ambient temperatures and increases with temperature by approximately 0.9%/K$^{(3)}$. The excited molecules can decay to ground state giving off light of a characteristic frequency (chemiluminescence) or can collide with any third body (M) and decay to ground state without chemiluminescence (quenching). The relative importance of the chemiluminescent and quenching reactions depends upon the temperature and the amounts and types of molecules available for quenching. If these factors are constant and the amount of O_3 present is large, the intensity of chemiluminescence is directly proportional to NO concentration.

Figure 1 is a simplified schematic diagram of a NO analyzer based upon this reaction scheme. A sample gas containing NO is metered into a reaction chamber at a constant rate by a suitable flow metering system. Ozone produced from O_2 is also metered into the reaction chamber at a constant rate. The O_2 flowrate is selected to produce a reaction chamber O_3 concentration many times the maximum anticipated NO concentration. Thus the reaction between NO and O_3 does not measurably deplete the O_3 concentration and the intensity of chemiluminescence is directly proportional to NO concentration in the sample gas. The chemiluminescent emission is filtered to remove extraneous light and directed upon a photomultiplier tube (PMT). The PMT output is amplified and suitably scaled to read out directly in concentration units (PPM). The amplifier zero offset and gain are adjustable to permit calibration with standard gases. High purity N_2 (free from NO) is used to set the zero offset. This allows the PMT dark current, which varies with PMT age and temperature, to be nulled out. A known concentration of NO in N_2 background gas is used to adjust the instrument gain or span.

Commercial CLAs are designed and constructed to maintain the variables affecting instrument calibration very close to constant. Calibration drift on state-of-the-art instruments is usually less than 3% of span per day. A CLA calibrated as described above will indicate the correct NO concentration (within about 1%) of any mixture of NO in N_2 within instrument range. However if the sample gas contains species other than NO or N_2, these gases could cause the instrument to read incorrectly.

There are four potential ways in which sample gas composition variations could alter CLA response to NO; these are:

- Depletion of O_3 by chemical reaction
- Chemiluminescence of gases other than NO within the optical filter band width
- Sample flowrate variations due to sample gas property changes
- Sample gas species with quenching efficiencies different from N_2

The first two items are not usually important in measurements of combustion products. However the last two items can cause significant variations in CLA calibrations.

The CLA measures the number of NO molecules entering the reaction chamber per unit time. If the sample gas flowrate is constant, the number of molecules of NO entering the reaction chamber per unit time is directly proportional to the NO concentration. The sample gas flowrate in many commercial CLAs is maintained constant by passing the sample gas through a capillary and regulating the capillary pressure drop. However, the volumetric flowrate through a capillary with fixed pressure drop is inversely proportional to the sample gas dynamic viscosity (μ). Thus sample gas compositions with viscosity different from that of N_2 will result in sample gas flowrates different from N_2 and therefore the CLA will not respond properly to NO. Sample gases with low viscosity will result in indicated NO concentrations greater than actual and vice versa.

The NO_2* produced by reaction of NO and O_3 can either decay to the ground-state producing chemiluminescence or transfer energy to other molecules (M) without chemiluminescence (quenching). Some quenching is unavoidable due to the finite probability of NO_2* molecules colliding with other molecules in the reaction chamber. The rate of the quenching reaction depends upon the amount and types of molecules in the reaction chamber. Reaction chamber pressure affects quenching by altering the mean free path and collision frequency. Low pressure tends to reduce quenching and several commercial CLAs operate with reaction chamber pressures less than 10 torr. The quenching reaction rate affects the intensity of chemiluminescence and hence variations in the quenching reaction rate will alter CLA response to NO.

The quenching reaction rate is significantly influenced by the type of molecules in the reaction chamber. Experimental evidence confirms that the rate of quenching increases with the number of degrees of freedom of the molecules present in the reaction chamber and varies substantially for gases commonly found in combustion products.(4) Mathews et al(5) recently compiled quenching data from several investigators.

The variations in chemiluminescent response to NO due to quenching and viscosity effects are generally of the same order of magnitude. However, the magnitude and direction of the effects vary for specific gases. For some gases such as H_2 and O_2 the combined effects of quenching and viscosity result in a greater error than for quenching alone. For other gases such as H_2O, CO_2 and Ar the error is reduced by inclusion of viscosity effects.

SECTION 3

EXPERIMENTAL PROCEDURE AND APPARATUS

Two CLAs were selected for evaluation:

- Beckman Model 951
- Thermal Electron Corporation (TECO) Model 10A

The Beckman analyzer utilizes an atmospheric reaction chamber. Sample gas and ozone flows are controlled by regulating the pressure drop across capillaries. Sample pressure is provided by an internal sample pump.

The TECO analyzer utilizes a subatmospheric pressure reaction chamber operating at nominally 9 torr. As with the Beckman analyzer, flowrates in the TECO are controlled by capillaries. A vacuum pump exhausts the reaction chamber and creates the pressure drop across the capillaries. The use of a subatmospheric reaction chamber adds considerable complexity to the instrument but reduces the importance of quenching thus increasing sensitivity to low NO concentrations.

The manufacturers' instructions for both CLAs include detailed operating information specifying the proper pressures, flowrates and calibration procedures. Filtering and drying the sample gas to a dewpoint less than operating temperature is required to prevent sample capillary blockage.

The operating procedure used by technicians in laboratory and field tests varies somewhat with sample train design and test conditions. Most commonly the instrument is utilized intact, operated according to the manufacturers' instructions and zeroed and spanned with N_2 and NO in N_2 respectively. This was the procedure utilized in this investigation. However, in tests of subatmospheric combustors, such as flat flames, a low reaction chamber pressure CLA (such as the TECO) is often used without the sample gas capillary. This allows the sample gas to pass directly from the probe to the reaction chamber without water removal. Sample flowrate is controlled by the probe tip which acts as a sonic flow orifice. The results of this investigation cannot be directly applied to CLAs operated in this manner.

Table 1 shows the gas mixtures tested in this investigation. These mixtures were prepared by blending high purity gases and mixtures of NO in N_2 or Ar with a precision gas flow metering system. Nitric oxide in N_2 span gases were prepared similarly so that inaccuracies in mixed gases supplied in cylinders could not affect the CLAs' relative responses to span gases and sample gases.

For each experiment in Table 1, the CLAs were adjusted to read correctly on N_2 with no NO and a mixture of NO in N_2. The instruments were then used to measure the concentrations of NO in the mixture compositions tested. The actual concentrations of NO in span and test gases were identical so that the ratios of NO measured in the test gases to actual NO concentrations were direct measurements of background gas composition effects. The CLAs' responses to N_2 zero and NO in N_2 span gases were checked after each datum point. Concentrations of O_2, CO and CO_2 in zero, span and test gases were also monitored as a check on metering system accuracy and to verify no leaks in the sampling train.

A schematic diagram of the experimental apparatus is shown in Figure 2. The only materials in contact with gas mixtures containing NO were stainless steel, glass and teflon. The total inaccuracy in the flowrate of each gas was less than 0.5%. Water vapor was added by bubbling some of the gases (O_2 and N_2) through distilled water. Contacting of the NO mixtures with O_2 and H_2O was controlled by maintaining the NO mixtures separate from the O_2 and H_2O. The two streams were blended immediately upstream of the instruments in a short length of teflon tubing. The instruments included Beckman and TECO CLAs and other instruments to measure O_2, CO, CO_2 and dewpoint.

All gases were high purity grade (99.97% or better) with the exception of CO (99.0%). NO was supplied as mixtures in N_2 and Ar (± 5% accuracy) to facilitate metering. All mixed gases were calibrated against a National Bureau of Standards (NBS) traceable mixture. To confirm the concentrations of NO in the test gas mixtures, several gas mixtures were analyzed utilizing the phenolydsulfonic acid (PDSA) method. The maximum deviation between calculated and PDSA measured concentrations was 3.0%.

SECTION 4

RESULTS

EXPERIMENT NO. 1 - BINARY BACKGROUND GASES

Figures 3 and 4 show the results of the binary background gas tests as the ratios of indicated to actual NO concentrations as functions of the concentrations of gases in the M/N_2 mixtures. As the concentration of gas M approaches zero, the ratio of indicated to actual concentration must approach 1.0 since 100% N_2 was the background gas used for spanning the instruments.

The results for all gases except H_2 at high concentrations show either negligible changes or decreases in the ratios of indicated to actual NO concentrations as the concentrations of the gases in the background mixtures increase. The results for CO and H_2 are similar for both CLAs. This is expected since quenching data(5) indicates that the relative quenching efficiency of CO, H_2 and N_2 are nearly the same. Carbon monoxide has essentially the same viscosity as N_2 and thus the viscosities of CO/N_2 mixtures are the same as N_2. This accounts for the negligible effects of CO concentration in the background gas on the ratios of indicated to actual NO concentrations. H_2 has a viscosity much smaller than N_2 and the viscosities of mixtures of H_2 in N_2 decrease rapidly as the concentrations of H_2 increase above 20%. This accounts for the increase in the ratio of indicated to actual NO concentration at high H_2 concentrations.

The results for the other binary background gas mixtures in Figures 3 and 4 can also be explained by examining the combined effects of viscosity related flowrate variations and quenching efficiency variations. For example, CH_4 has a viscosity less than N_2 and the viscosity related flowrate variations with CH_4/N_2 mixtures tend to increase the ratio of indicated to actual NO concentrations as the concentration of CH_4 increases. However, since CH_4 has more degrees of freedom than N_2, its quenching efficiency should be greater tending to decrease the ratio of indicated to actual NO concentration as the concentrations as the concentration of CH_4 increases. However, since CH_4 has more degrees of freedom than N_2, its quenching efficiency should be greater tending to decrease the ratio of indicated to actual NO concentration as the concentration of CH_4 increases. The results in Figure 3 show that the combined effects of quenching and viscosity variations produce a nearly flat response with the TECO. With the Beckman, the quenching efficiency effects are much larger (due to the higher reaction chamber pressure) and over compensate the viscosity effects to produce a decrease in ratio of indicated to actual NO concentration as CH_4 concentration increases.

EXPERIMENT NO. 2 - LEAN COMPLETE COMBUSTION PRODUCTS (DRY)

Figure 5 shows the results of tests on the simulated complete dry combustion products from burning C and CH_4 in air. These background gas mixtures contained O_2, CO_2 and N_2. In all tests the ratios of indicated to actual NO concentrations were less than 1.0. The TECO generally indicated NO concentrations closer to the actual levels than the Beckman. This is consistent with the results of experiment No. 1. For both instruments, the simulated combustion products from C exhibit more deviation than those from CH_4. This is a direct result of the higher CO_2 concentration in the simulated combustion products from C.

These experiments were conducted with two concentrations of NO in the sample and span gas mixtures. Figures 5A and B show the results for 200 ppm NO for C and CH_4 fuels. Figure 5C compares the results for C as the fuel with 100 and 200 ppm NO and shows that the ratio of indicated to actual NO concentration is independent of the NO doping level.

EXPERIMENT NO. 3 - LEAN COMPLETE COMBUSTION PRODUCTS (WET)

The previous experiments were conducted with dry sample gas mixtures prepared by blending dry compressed gases from cylinders. The dewpoints of these mixtures were about 205K. In laboratory and field emissions tests the combustion products generally contain several percent H_2O and the dewpoint may be as high as 350K. The usual procedure is to draw the sample gas through a water/ice bath to remove most of the H_2O and reduce the dewpoint beneath ambient temperature. This prevents condensation in the sample capillary and the associated plugging.

In this experiment the water vapor was added to the dry simualted combustion products to produce dewpoints in the range of 275 to 294K. Figure 6 shows the results for C burning in air at 100, 250 and 500% theoretical air. At each stoichiometry increasing the dewpoint decreased the ratio of indicated to actual NO concentration. The effect was small for the TECO (1.0 to 2.0%) but substantial for the Beckman (up to 6.0%)

EXPERIMENT NO. 4 - INCOMPLETE LEAN COMBUSTION PRODUCTS (DRY)

The method of simulating incomplete combustion products utilized in these tests was to allow 20% of the CO_2 in the simulated complete combustion products to be reduced to CO and O_2. Figure 7 shows the results for simulated combustion products burning C in air assuming complete and incomplete combustion. The TECO's performance is essentially unaffected while the Beckman's improves with incomplete combustion. This is a result of the decrease in CO_2 concentration.

EXPERIMENT NO. 5 - RICH COMBUSTION PRODUCTS (DRY)

The simulated rich combustion product mixtures contained CO, CO_2, H_2 and N_2. The results of those tests are shown in Figure 8. As with the lean combustion products, the TECO generally indicated closer to the actual NO concentration than the Beckman. Largest deviations were at near stoichiometric conditions with C as the fuel. Under very rich conditions (50% theoretical air) with CH_4 as the fuel, both CLAs indicated slightly higher than the actual concentation of NO. At 50% theoretical air the concentration of H_2 is over 17% and the binary background gas tests demonstrated that high concentrations of H_2 result in indicated NO concentations greater than actual.

It should be noted that the products of combustion from practical combustors operated fuel rich will generally be different from the compositions utilized in these tests. These simulated combustion product compositions were selected for simplicity and to give an approximate indication of the CLA performance sampling rich products.

EXPERIMENT NO. 6 AND 7 - COMBUSTION PRODUCTS IN Ar ATMOSPHERES (DRY)

In experiments involving combustion of fuels containing bound nitrogen it is difficult to differentiate between NO formed from atmospheric N_2 and NO formed from nitrogen bound in the fuel. Several investigators have recently combusted fuels containing bound nitrogen in an oxidant containing only O_2, CO_2 and Ar to eliminate NO formation from N_2. The oxidant mixtures most commonly used are 21% O_2 balance Ar and 21% O_2, X% CO_2 balance Ar. Carbon dioxide is sometimes added to adjust the flame temperature to match the flame temperature produced with air as the oxidant. The concentration of CO_2 required is usually 20%.

Experiments 4 and 5 were repeated with O_2/Ar and O_2/CO_2/Ar as the oxidants and the results are shown in Figures 9 and 10. The results for lean combustion products obtained with the TECO are essentially independent of stoichiometry, oxidant (O_2/Ar or O_2/CO_2/Ar) and fuel (C or CH_4). However, while similar results for combustion of fuels in air gave ratios of indicated to actual NO concentrations of 0.95 to 0.99, these results are much lower (0.82 to 0.87).

The results for lean combustion products obtained with the Beckman are also lower than comparable results obtained with air as the oxidant but the differences are smaller than with the TECO. The Beckman results are also affected by the CO_2 content of the oxidant; increasing CO_2 concentration decreases the ratio of indicated to actual NO concentrations.

The results of the rich combustion products tests shown in Figure 10 show the same general trends as the lean tests: the TECO response is nearly constant independent of stoichiometry and oxidant under rich conditions and the Beckman results are very sensitive to the concentration of CO_2 in the oxidant.

EXPERIMENT NO. 8 - OFF DESIGN POINT CLA OPERATION

All of the previous experiments were conducted with the CLAs operated strictly according to the manufacturers' instructions. Figure 11 shows the results of operating the CLAs under other conditions. Simulated combustion products from burning C in air and O_2/Ar oxidants were utilized and the CLAs were zeroed, spanned and used to measure these sample gases with the operating parameters set at several conditions. Figure 11 shows the ranges of instrument response observed as the independent parameters were varied. In all cases, variations in the operating parameters resulted in only minor changes (± 3%) in instrument response.

SECTION 5

DISCUSSION

The results of the experiments discussed above show that commercial CLAs generally indicate NO concentrations lower than actual when spanned with mixtures of NO in N_2 and used to sample NO in combustion products. The errors introduced by neglecting sample background gas composition variations cover the following ranges:

COMBUSTION PRODUCTS FROM FUEL AND:	ERROR % TECO	ERROR % BECKMAN
21% O_2/N_2	+1 to -5	+2 to -11
21% O_2/Ar	-11 to -16	-6 to -14
21% O_2/21% CO_2/Ar	-12 to -15	-15 to -20

These results apply directly to the two CLAs tested but are probably representative of the performance of other instruments of similar design as well. Both instruments utilize capillaries to control sample flowrates. The TECO reaction chamber operates at approximately 9 torr while the Beckman reaction chamber operates at atmospheric pressure.

The gases responsible for the majority of the errors are CO_2, H_2O, O_2 and Ar. Each of these gases decrease the CLA's sensitivity to NO. Carbon dioxide is often present at high concentrations in combustion products and accounts for the majority of the errors at near stoichiometric conditions. Water vapor has a much higher quenching efficiency than N_2. At the low H_2O concentrations typical of combustion products dried in an ice bath, the quenching effects far outweigh the effects of viscosity. Sample dewpoint variations can change CLA response to NO by several percent. For O_2, the effects of viscosity an quenching variations are additive and this combined with the high concentrations of O_2 present in lean combustion products results in errors as high as 4%.

The effects of viscosity and quenching variations are opposite for Ar. In the CLAs tested here, the viscosity related variations over compensated the quenching variations resulting in a decrease in CLA sensitivity to NO with increasing Ar concentration. In the experiments reported in reference 5, the sample flowrate was maintained constant and the results did not include the viscosity related flowrate variations present in these experiments. This accounts for the reported opposite effect of Ar on CLA response to NO. In combustion experiments utilizing O_2/Ar or O_2/CO_2/Ar as the oxidant, the concentration of Ar in combustion products is high and results in CLA errors as high as 20%.

The variations in CLA response due to background gas composition variations were generally smaller with the TECO than with the Beckman except for Ar. Based upon these results a low reaction chamber pressure CLA such as the TECO would be preferred to monitor products of combustion of fuels burned in air. However, the choice of instruments for experiments involving O_2/Ar or O_2/CO_2/Ar oxidants is unclear. The following example illustrates these points.

A fuel containing bound nitrogen is burned in three oxidants: air, O_2/Ar and O_2/CO_2/Ar. It is assumed that 500 ppm of NO are formed from fuel bound N_2 independent of oxidant composition. It is further assumed that an additional 500 ppm of NO are formed from N_2 when the fuel is burned in air. Ideally, the experimental results would indicate 1000 ppm in the air experiment and 500 ppm in both Ar experiments. The thermal NO could then be calculated as the difference in NO concentrations (500 ppm).

Table 2 shows the results which would be obtained in this experiment utilizing the TECO and Beckman CLAs but without correcting the results for background gas composition variations. The fuel was assumed to be C burning at 100% theoretical oxidant and the instrument response was taken from the results in section 4.

In the air experiments the TECO reads closer to the correct concentration. However, with the O_2/Ar oxidant both CLAs indicate incorrectly by the same amount. The thermal NO concentrations calculated by subtracting the NO concentrations are in error by equal amounts for both CLAs but the errors are in opposite directions. With the O_2/CO_2/Ar oxidant the TECO reads closer to the correct concentration. However, the Beckman yields better results for the thermal NO. This example shows no clear cut advantage for either instrument design.

The results of this study can be used to correct the results of NO emission tests for the effects of background gas composition variations. Accurate corrections can be made if:

- The CLA utilized in the emission tests was one of those tested here
- The CLA was operated according to the manufacturer's recommendations
- The combustion product compositions are known

Figure 12 shows the application of the results of this study to an actual NO emission test conducted at Energy and Environmental Research Corporation. A No. 6 oil was fired in a bench scale furnace over a range of excess O_2 with air and $O_2/CO_2/Ar$ oxidants. Nitrogen oxides (NO_x) were measured with a TECO CLA equipped with a stainless steel converter to reduce NO_2 to NO. The indicated NO_x concentrations were corrected for background gas composition variations by applying the results in section 4. The C and CH_4 data were interpolated to account for the oil's H/C ratio and the results obtained for 21% O_2/21% CO_2/Ar were used (neglecting the difference between 20 and 21% CO_2 in the oxidant). Application of these results to the experimental data slightly increases the NO_x concentration for combustion in air and substantially increases (60 ppm) the NO_x concentration for combustion in the oxidant containing Ar. The conversion of fuel nitrogen to NO_x is higher and the thermal NO_x formation is lower than if the effects of background gas composition variations had been neglected.

SECTION 6

RECOMMENDATIONS

In many laboratory and field emissions tests the variability in operating conditions and other factors introduce errors of the same order of magnitude or larger than the errors produced by background gas composition variations. Under these conditions it is recommended that the NO concentrations indicated by the CLAs be used directly without corrections recognizing that the results will tend to be low by a few percent.

If the experimental errors in the emissions tests are small compared to the errors produced by background gas composition variations, the indicated NO concentrations should be corrected as discussed in the previous section. However the results of this investigation can only be applied to CLAs designed and operated similar to those tested. In low pressure flat flame experiments where the CLA sample gas metering system (capillary) is replaced by a different type of metering system, the effects of background gas composition variations on sample flowrate may be significantly different. Under these conditions the results of this investigation cannot be applied. It is recommended that either the effects of background composition variations on sample gas flowrate be evaluated and quenching data such as Reference 5 be applied, or the overall effects of background composition variations be emperically determined as in this investigation.

As an alternative to correcting the indicated NO concentrations, the CLA could be operated so as to minimize the effects of background gas composition variations. Three methods for accomplishing this are to:

- Calibrate the CLA with NO in a background gas similar to the anticipated combustion products
- Dilute the sample with a known amount of N_2
- Dry the sample to a low dewpoint

Calibrating the CLA with NO in a background gas with a composition identical to the combustion products to be sampled would eliminate these problems. However, the concentration of NO in the mixture must be accurately known. Some gas mixture suppliers determine the concentration of NO in their mixtures by using a CLA. This introduces errors similar to calibrating the laboratory CLA on NO in N_2.

If the sample gas is diluted with a large amount of N_2, variations in sample gas compositions will have less effect on the flowrate into the reaction chamber and quenching. For this technique to be effective the dilution factor must be large (such as 10/1) and precisely known independent of sample gas composition variations. This accurate dilution is difficult to achieve in practice and has the further disadvantage of reducing the overall sensitivity of the CLA by the dilution factor.

The sample gas must be dried to a dewpoint less than the CLA operating temperature to avoid plugging the sample capillary with condensation. However at 293K dewpoint the sample gas contains 2.3% H_2O vapor and as a result the CLA will indicate less than the actual NO concentration due to background and dilution effects. Lowering the dewpoint to 273K reduces the H_2O vapor concentration to 0.60% and reduces the error in indicated NO concentration.

In experiments involving combustion products of fuels in air, a low pressure reaction chamber CLA such as the TECO is preferred. However in experiments involving combustion in O_2/Ar or O_2/CO_2 Ar oxidants, high and low reaction chamber pressure CLAs perform equally well.

Small variations in CLA operating conditions such as adjustment of the sample gas or ozone flowrates and changes in the reaction chamber pressure do not have any clear advantages in reducing the effects of background gas composition variations. However if the reaction chamber pressure is maintained low, the sample gas flowrate is maintained constant and the ratio of O_2 to sample gas flowrates in high, the effects of background gas composition variations could be significantly reduced.

REFERENCES

1. Clough, P.N., and Thrush, B.A. Mechanism of Chemiluminescent Reaction Between Nitric Oxide and Ozone. Transactions of the Faraday Society, Vol. 63, 1967. pp. 915.

2. Fontijn, A., Sabadell, A.J., Ronco, J. Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone. Analytical Chemistry, Vol. 42, 1970. pp. 575.

3. Niki, H., Warnick, A. and Lord, R. An Ozone - NO Chemiluminescence Method for NO Analysis in Piston and Turbine Engines. In: Proceedings of Automotive Engineering Congress. Detroit, Michigan, 1971. pp. 246.

4. Maahs, H.G. Interference of Oxygen, Carbon Dioxide and Water Vapor on the Analysis for Oxides of Nitrogen by Chemiluminescence. NASA Technical Memorandum NASA TM X-3229. August 1975.

5. Mathews, R.D., Sawyer, R.F. and Schefer, R.W. Interferences in Chemiluminescent Measurement of NO and NO_2 Emissions from Combustion Systems. Environmental Science and Technology, Vol. 11, 1977. pp. 1092.

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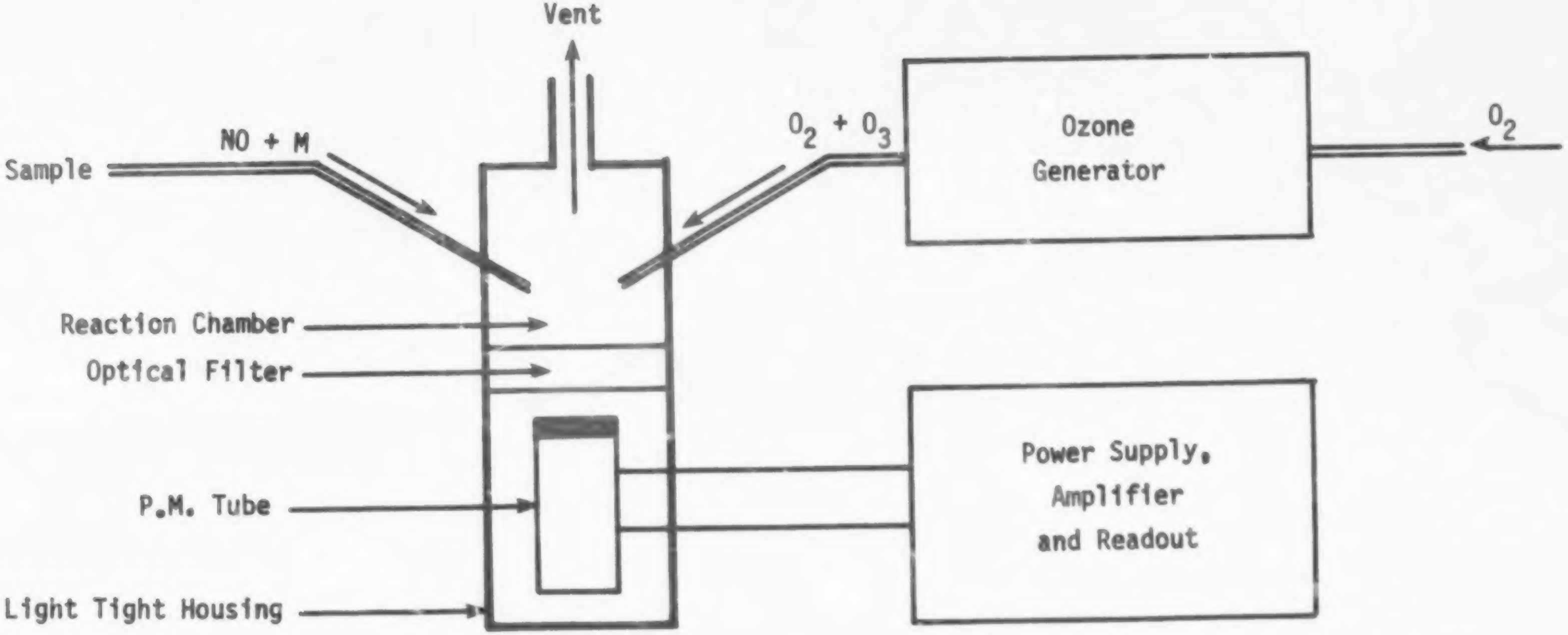
Vent
Sample
NO + M
O_2 + O_3
Ozone Generator
O_2
Reaction Chamber
Optical Filter
P.M. Tube
Light Tight Housing
Power Supply, Amplifier and Readout

Figure 1. Chemiluminescent Measurement of NO.

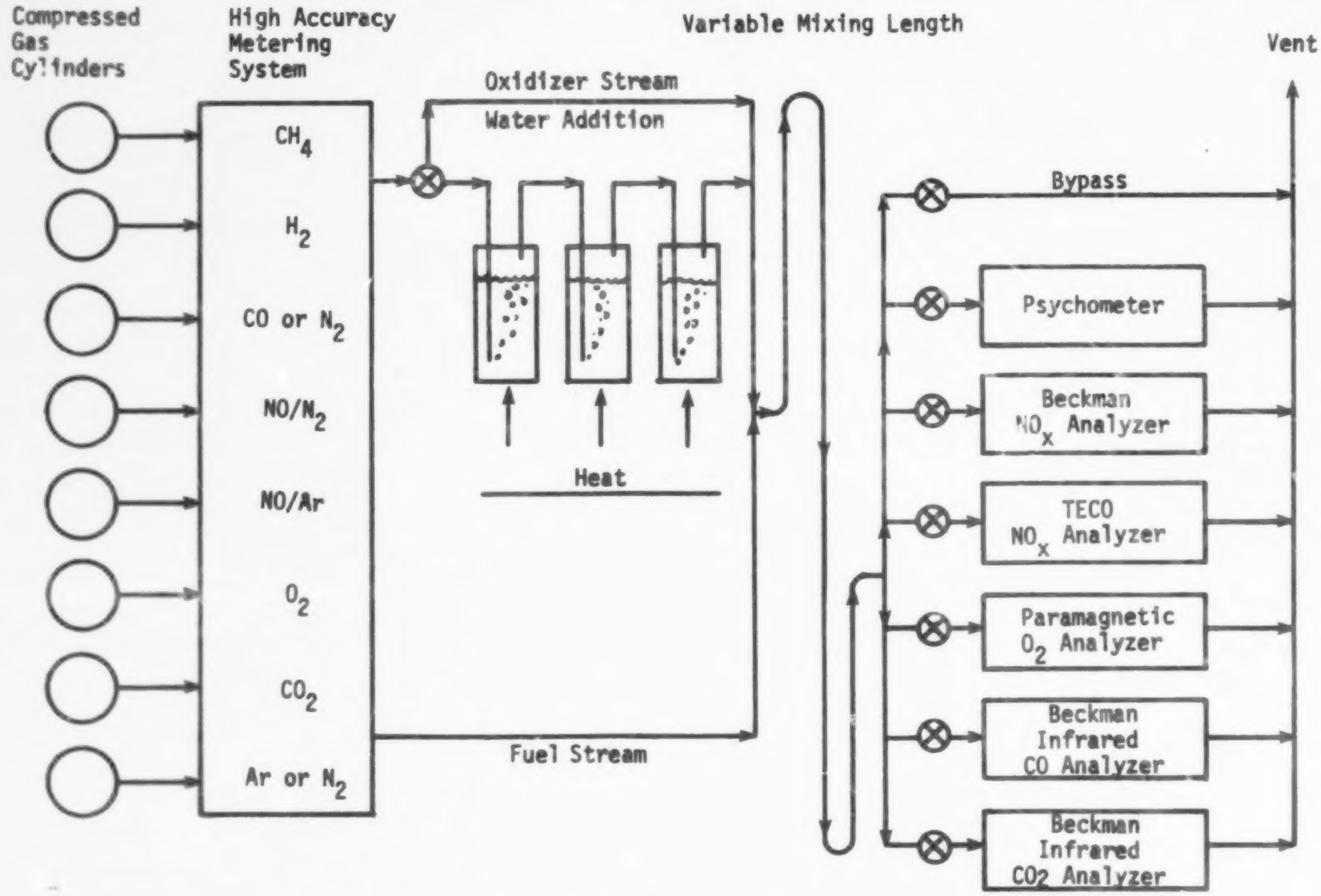
Compressed Gas Cylinders
High Accuracy Metering System
Variable Mixing Length
Vent
Oxidizer Stream
Water Addition
CH4
H2
CO or N2
NO/N2
NO/Ar
O2
CO2
Ar or N2
Heat
Fuel Stream
Bypass
Psychometer
Beckman NOx Analyzer
TECO NOx Analyzer
Paramagnetic O2 Analyzer
Beckman Infrared CO Analyzer
Beckman Infrared CO2 Analyzer

Figure 2. Experimental Apparatus.

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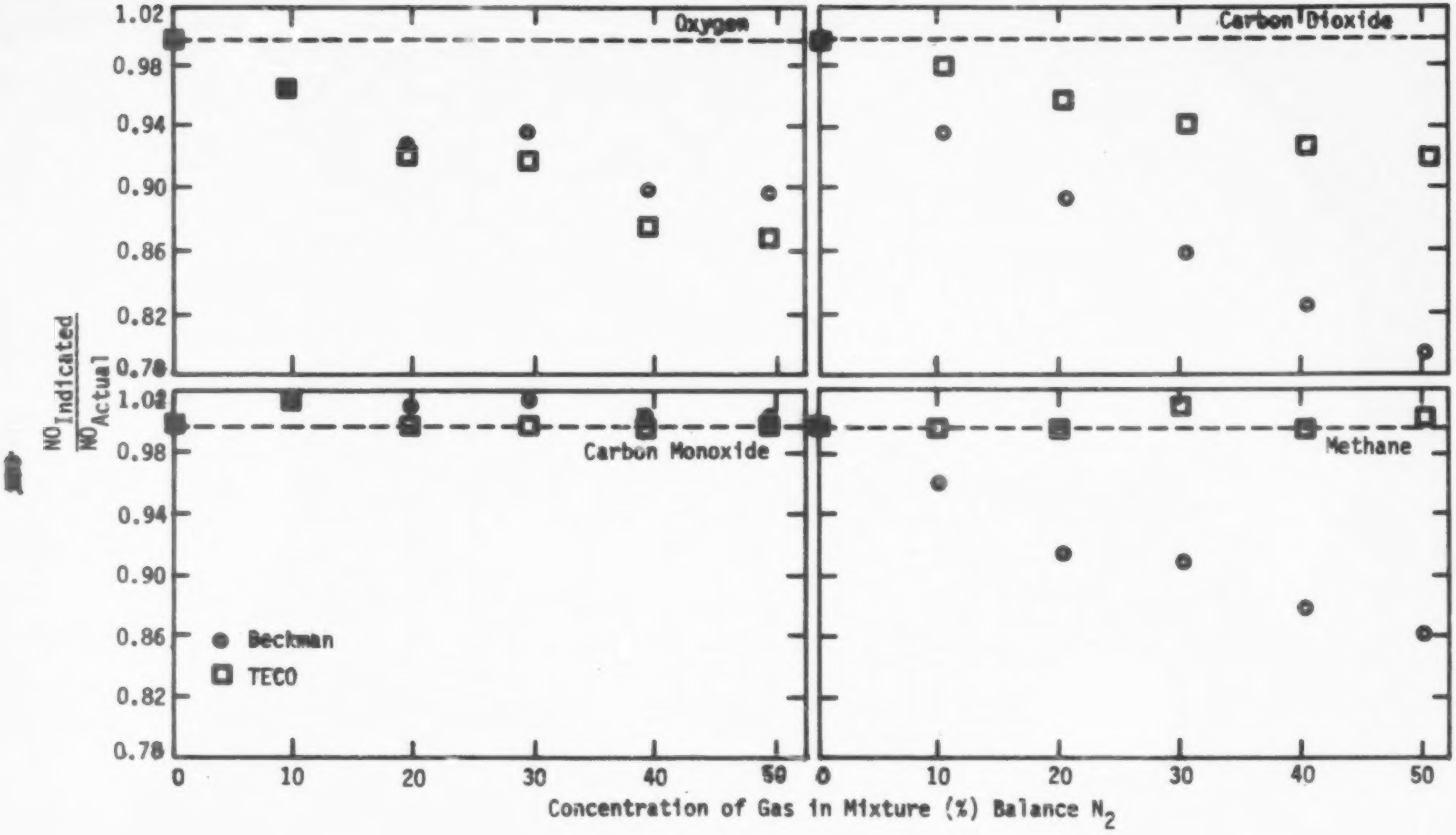

Figure 3. Experiment No. 1: Binary Background Gases.

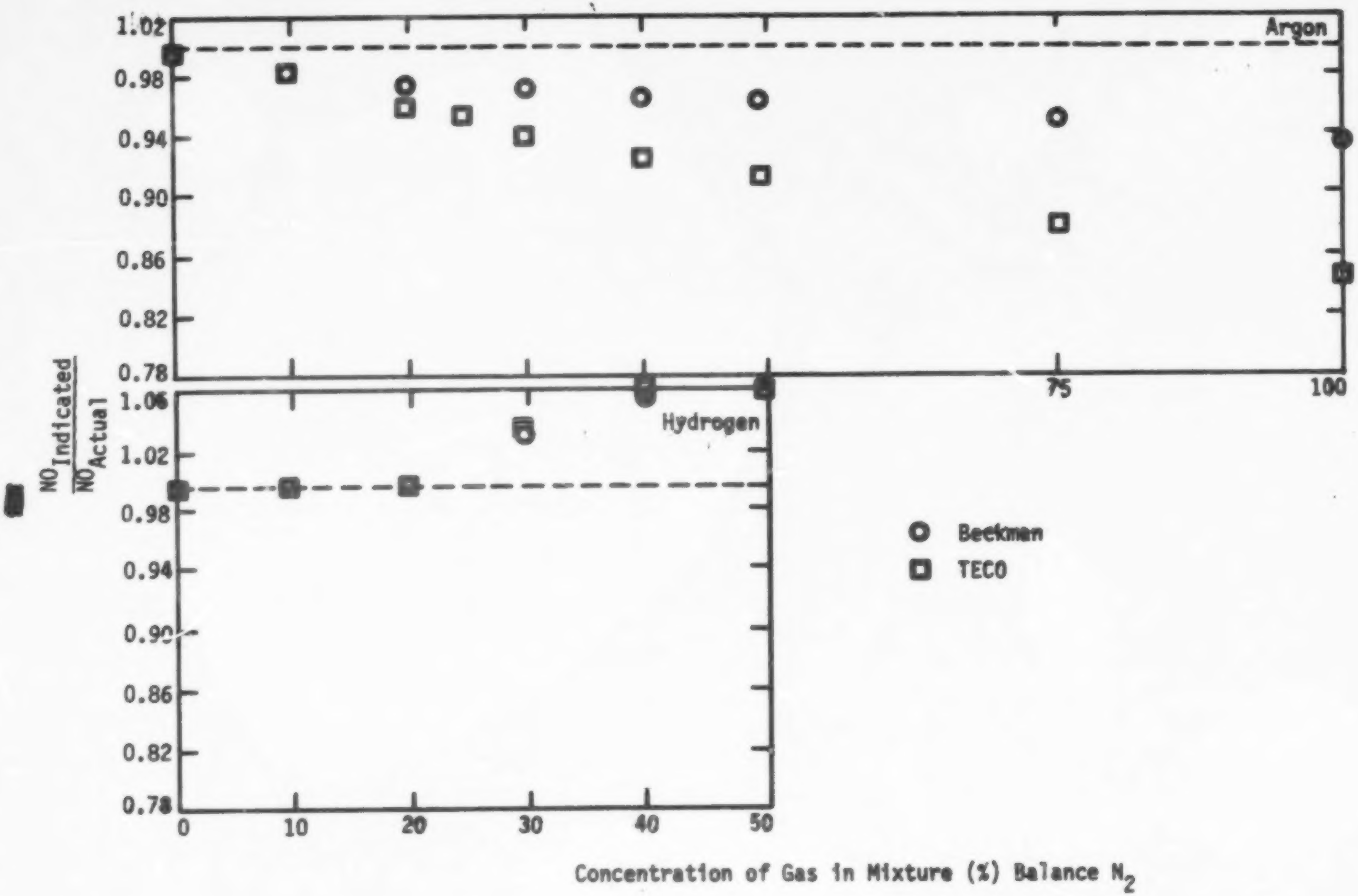

Figure 4. Experiment No. 1 (continued): Binary Background Gases.

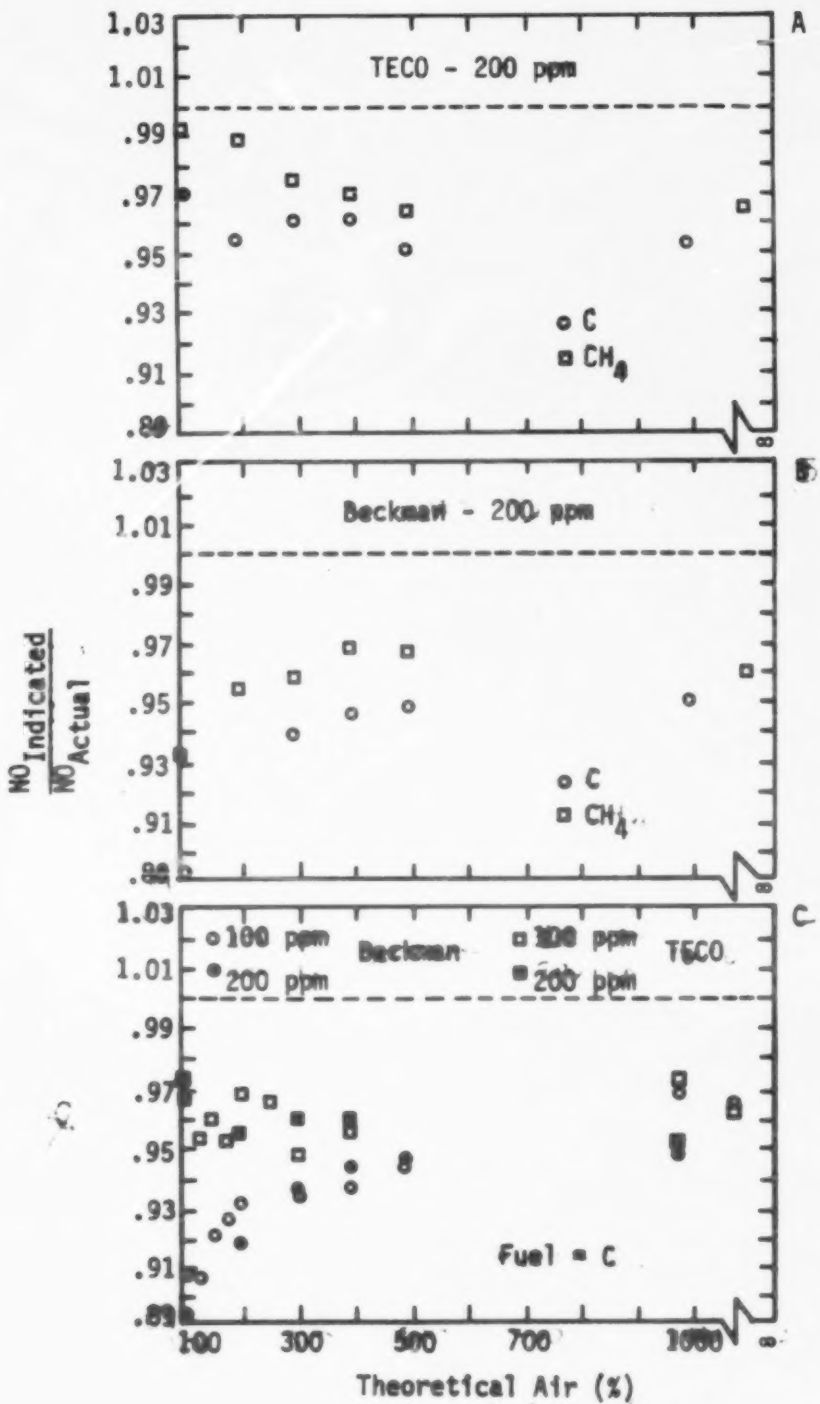

Figure 5. Experiment No. 2: Lean Complete Combustion Products Burning Fuels in Air (dry).

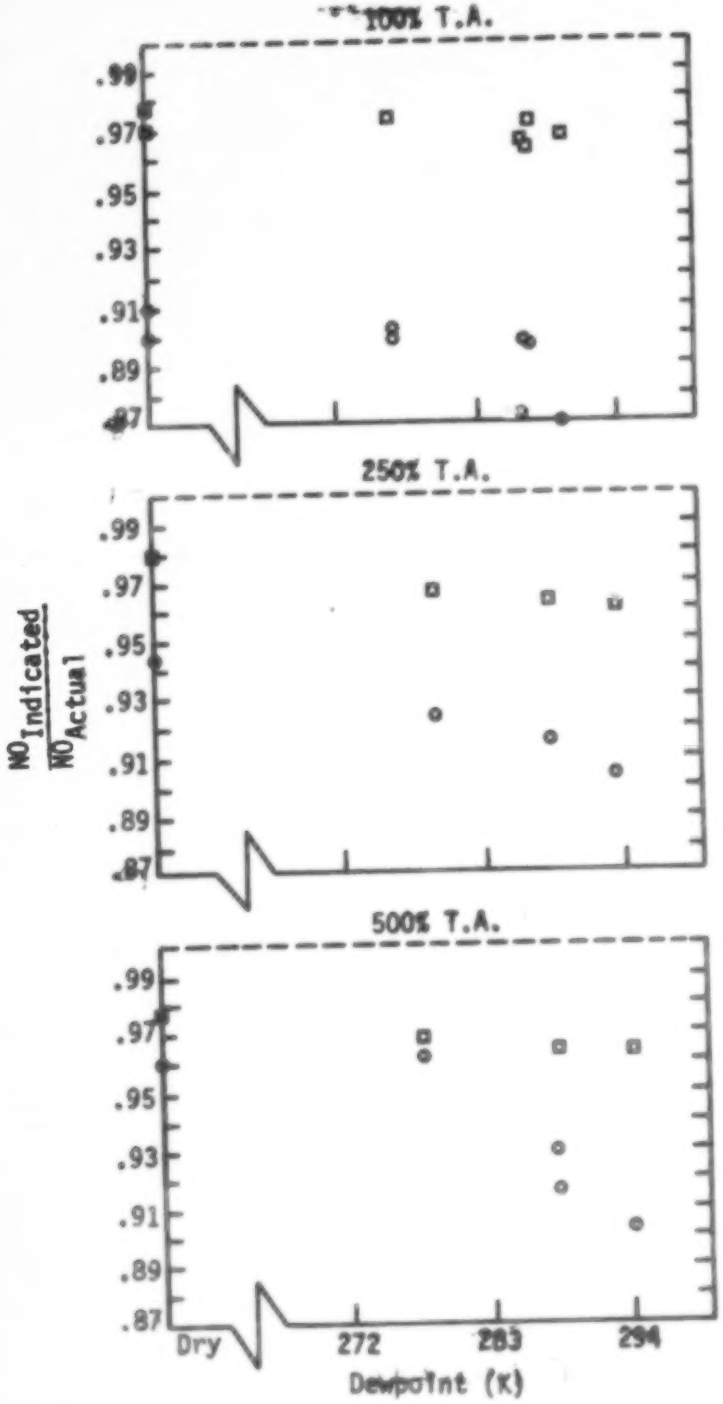

Figure 6. Experiment No. 3: Lean Complete Combustion Products from Burning C in Air (wet).

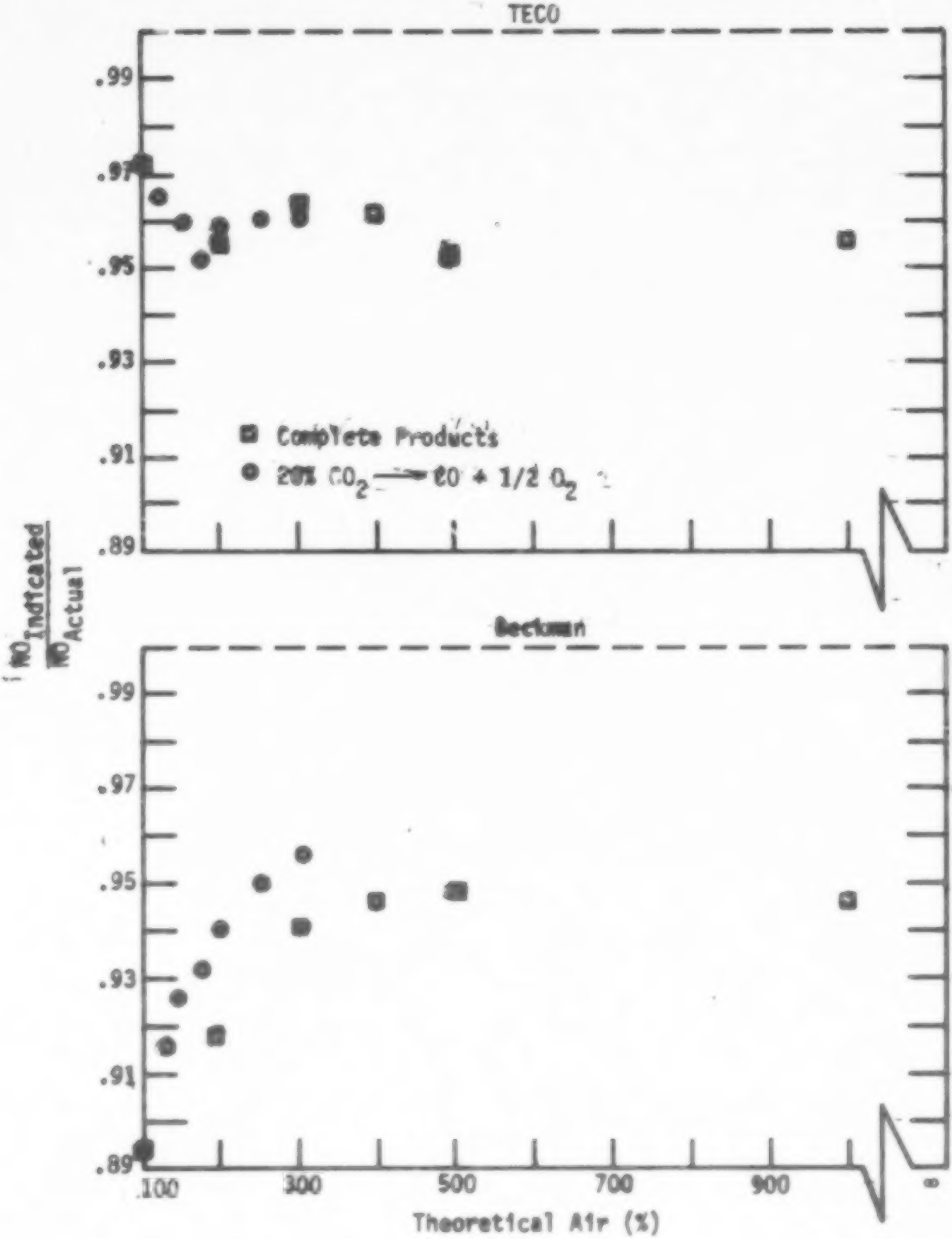

Figure 7. Experiment No. 4: Incomplete Lean Combustion Products Burning C in Air (dry).

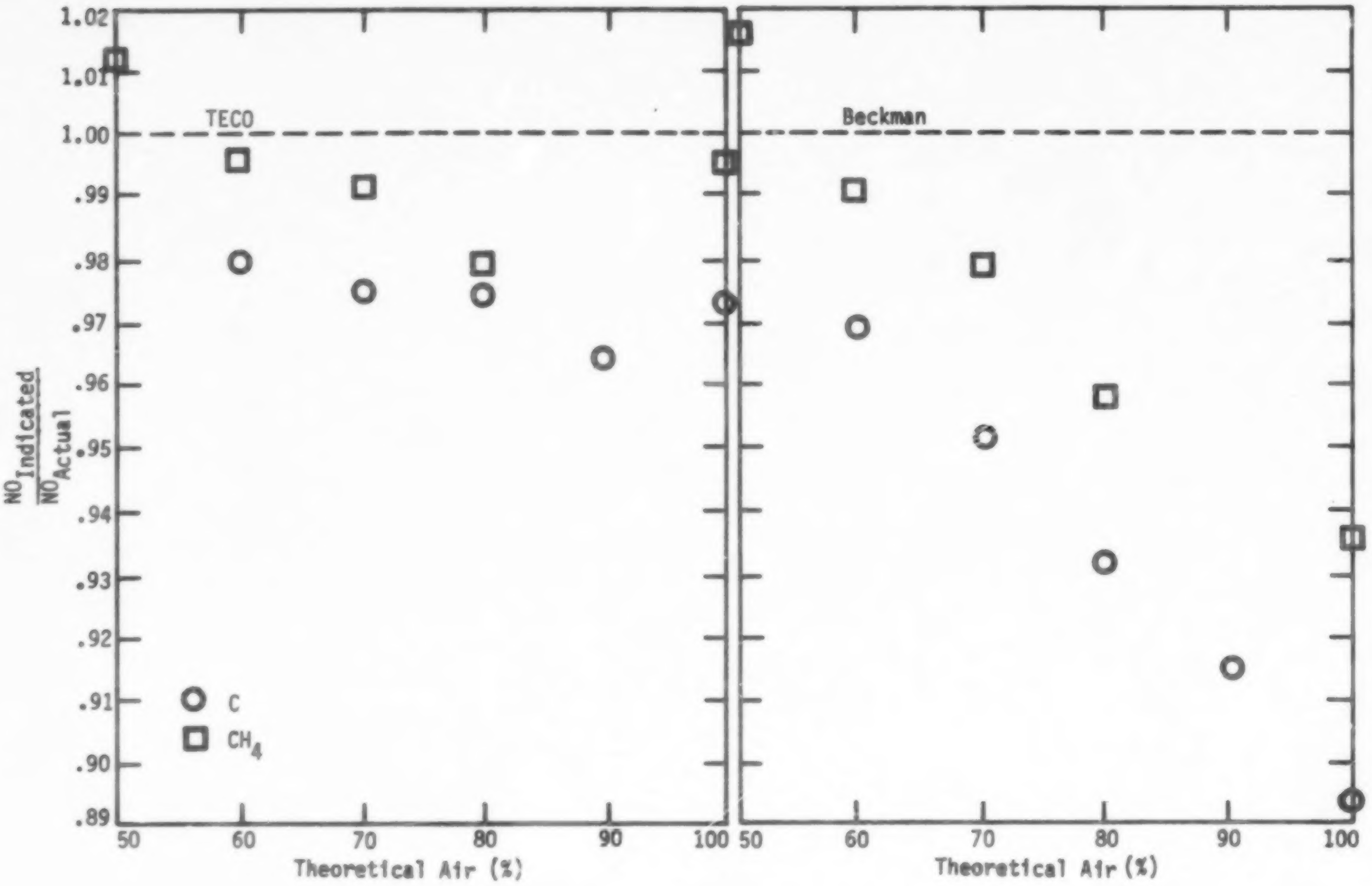

Figure 8. Experiment No. 5: Rich Combustion Products Burning Fuels in Air (dry).

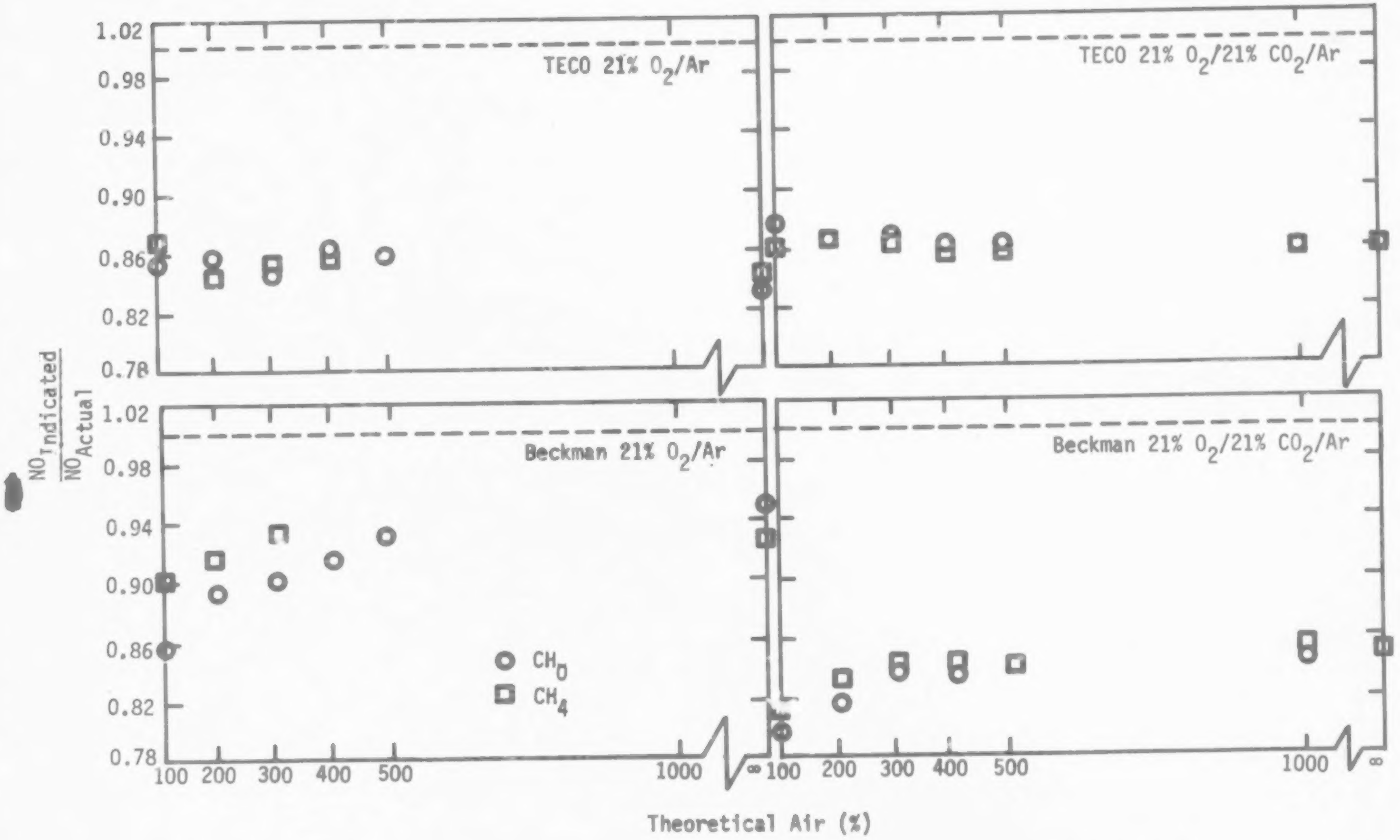

Figure 9. Experiment No. 6: Lean Complete Combustion Products Burning Fuels in O_2/A and O_2/CO_2/A Oxidants (dry).

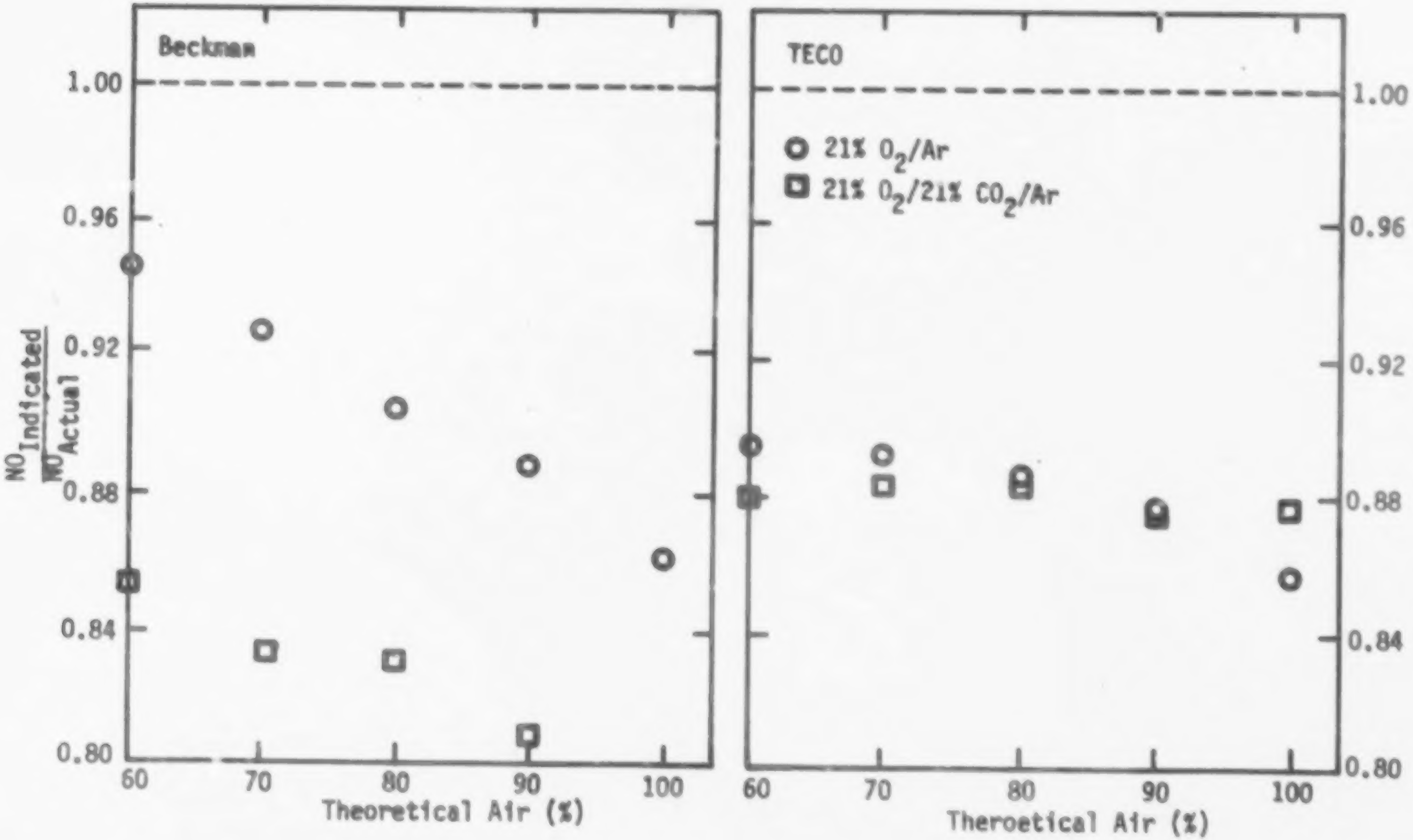

Figure 10. Experiment No. 7: Rich Combustion Products Burning C in O_2/A and O_2/CO_2/A Oxidants (dry).

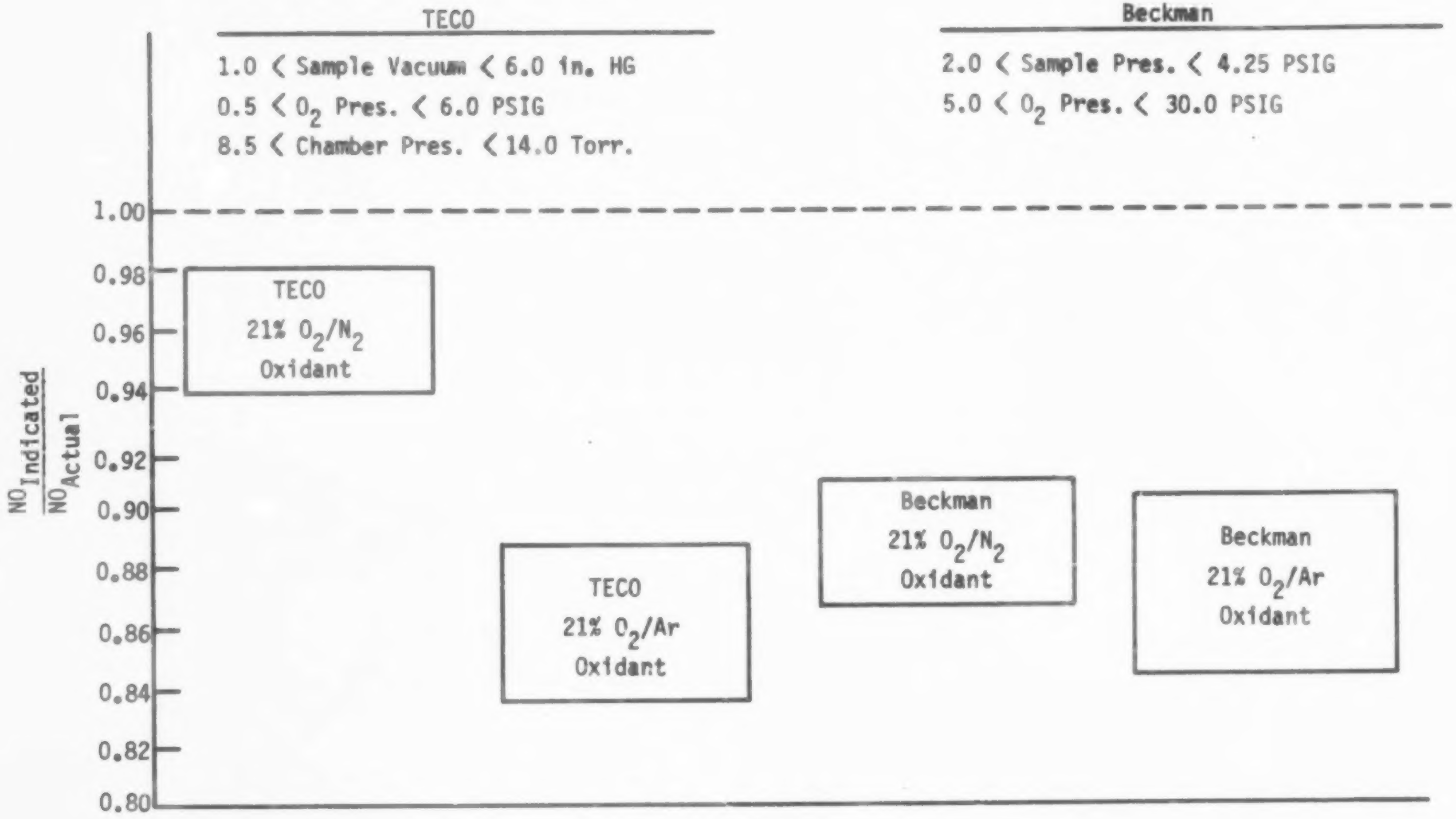

Figure 11. Experiment No. 8: Off Design Point CLA Operation Burning C at 125% Theoretical Oxidant (dry).

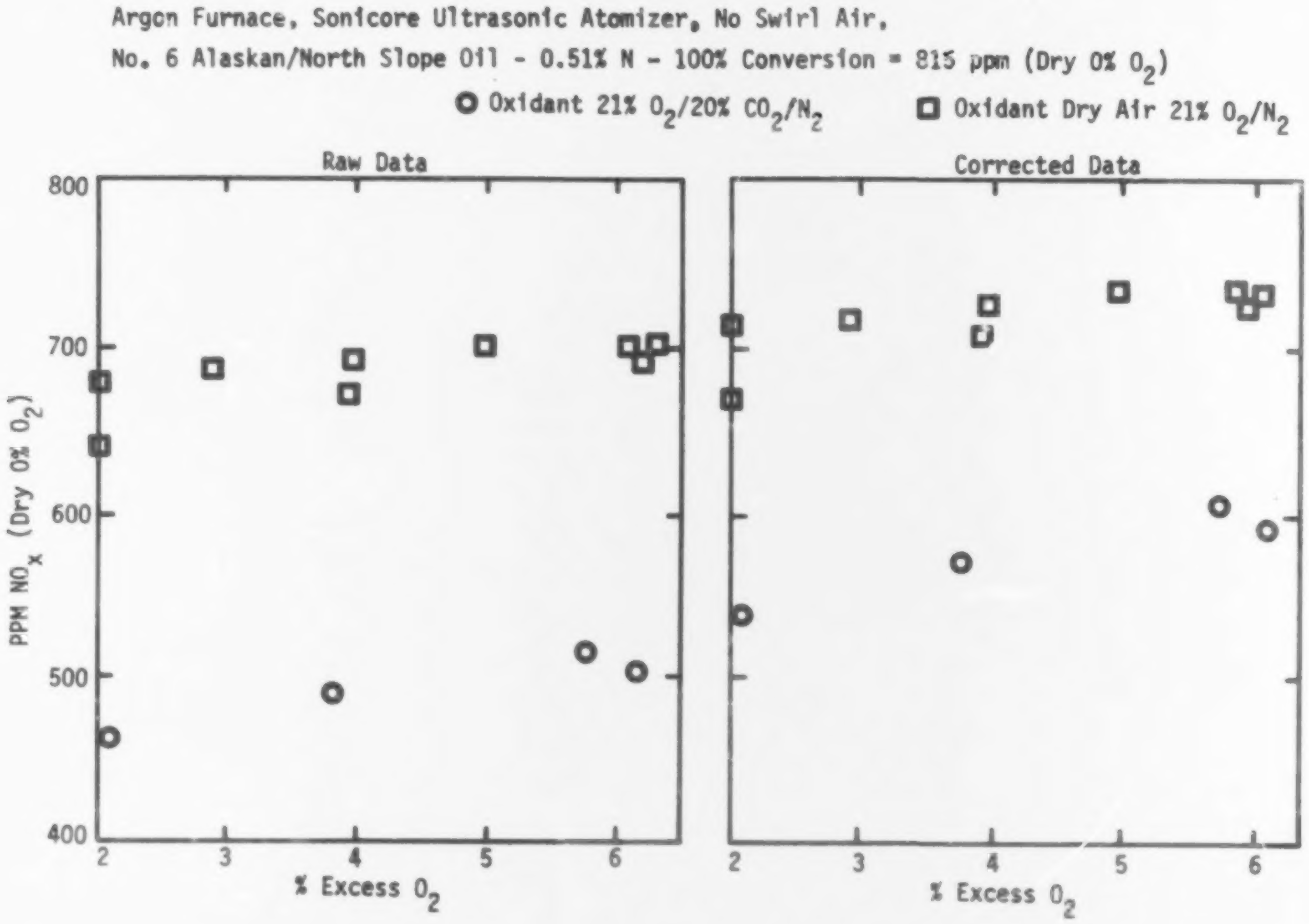

Figure 12. Example: Correcting Data for Background Gas Composition.

TABLE I. TEST MATRIX

EXPERIMENT NUMBER	CONDITIONS SIMULATED	FUELS	OXIDANTS	STOICHIOMETRY % T.A.	COMMENTS
1	**Binary Background Gases**				O_2,CO,CO_2,CH_4,H_2 or A in N_2
2	Lean Complete Combustion Product - Dry	C, CH_4	21% O_2/N_2	100 - ∞	
3	Lean Complete Combustion Product - Wet	C	21% O_2/N_2	100,250 500	Dry to 294 K Dewpoint
4	Lean Incomplete Combustion Product - Dry	C	21% O_2/N	125 - 300	20% $CO_2 \rightarrow CO + 1/2\ O_2$
5	Rich Combustion Product - Dry	C, CH_4	21% O_2/N_2	50 - 100	$[O_2] = 0$, Relative C and H Stoichiometries Equal, No Soot or $H_x C_y$
6	Lean Complete Combustion Product - Dry	C, CH_4	21% O_2/A 21% O_2/21% CO_2/A	100 - ∞	
7	Rich Combustion Product - Dry	C	21% O_2/A	60 - 100	$[O_2] = 0$, Relative C and H Stoichiometries Equal, No Soot or $H_x C_y$
8	Lean Complete Combustion Product - Dry	C	21% O_2/N_2 21% O_2/A	125	Instruments Operated off Design Points

TECHNICAL REPORT DATA

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16. ABSTRACT The proceedings document the approximately 50 presentations made during the symposium, March 5-8, 1979, in San Francisco. Sponsored by the Combustion Research Branch of EPA's Industrial Environmental Research Laboratory-RTP, the symposium dealt with subjects relating both to developing improved combustion technology for the reduction of air pollutant emissions from stationary sources, and to improving equipment efficiency. The symposium was in seven parts, and the proceedings are in five volumes: I. Utility, Industrial, Commercial, and Residential Systems; II. Advanced Processes and Special Topics; III. Stationary Engine and Industrial Process Combustion Systems; IV. Fundamental Combustion Research and Environmental Assessment; and V. Addendum. The symposium provided contractor, industrial, and government representatives with the latest information on EPA inhouse and contract combustion research projects relating to pollution control, with emphasis on reducing NOx while controlling other emissions and improving efficiency.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Air Pollution	Gas Turbines	Air Pollution Control	13B	13G
Combustion	Nitrogen Oxides	Stationary Sources	21B	07B
Field Tests	Efficiency	Environmental Assessment	14B	
Assessments	Utilities			
Combustion Control	Industrial Processes	Combustion Modification		
Fossil Fuels		Trace Species	21D	13H
Boilers	Hydrocarbons	Fuel Nitrogen	13A	07C

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